AL/EQ-TR-1996-0035

ARMSTRONG LABORATORY

CHAMBER STUDIES OF PHOTOLYSIS AND HYDROXYL RADICAL REACTIONS OF TRIFLUOROIODOMETHANE

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April 1996

Final Technical Report for Period June 1994 - July 1995

AIR FORCE MATERIEL COMMAND
TYNDALL AIR FORCE BASE, FLORIDA 32403-5323

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1. Report Date (dd-mm-yy)
30 APR 96

2. Report Type
Final

3. Dates covered (from... to)
JUN 94 to JUL 95

4. Title & subtitle

Chamber Studies of Photolysis and Hydroxyl Radical Reactions of Trifluoroiodomethane

5a. Contract or Grant #

F08635-93-C-0020

5b. Program Element # 62202F

5c. Project # 1900

5d. Task # S402

5e. Work Unit #

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8. Performing Organization Report #

9. Sponsoring/Monitoring Agency Name & Address
AL/EQS-OL
139 Barnes Drive, Suite 2
Tyndall AFB FL 32403-5323

10. Monitor Acronym

11. Monitor Report #
AL/EQ-TR-1996-0035

12. Distribution/Availability Statement

Distribution statement A approved for public release.
Distribution is unlimited.

13. Supplementary Notes Principal Investigator: Stewart J. Markgraf
Project Manager: Maj Floyd L. Wiseman

14. Abstract

Decay rate measurements were conducted in Teflon chambers for the photolysis and hydroxyl radical reactions of trifluoroiodomethane (CF3I). Photolysis studies were conducted outdoors, and results showed that photolysis of CF3I is dependent upon cloud cover. Half-lives for CF3I photolysis ranged from a few days to a few weeks. Hydroxyl radical rate studies were conducted by generating the hydroxyl radicals in situ using standard techniques. CF3I decay was monitored using standard spectrometric techniques. Results of the hydroxyl studies were poor due to extensive detection interferences and side reactions, although results indicated that photolysis is a more significant degradation pathway for CF3I than the second-order reaction with hydroxyl.

15. Subject Terms
CF3I; photolysis; hydroxyl radicals; product studies; decay rates

Security Classification of					
16. Report	17. Abstract	18. This Page	19. Limitation of Abstract	20. # of Pages	21. Responsible Person (Name and Telephone #)
Unclassified	Unclassified	Unclassified	Unlimited	42	Maj Floyd L. Wiseman (904)283-6288 DSN 523-6288

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PREFACE

This final report was prepared by the Environics Directorate, 139 Barnes Drive, Suite 2, Tyndall Air Force Base, Florida, 32403-5323. The work was conducted on site at the Environics Laboratory by Applied Research Associates under Contract Number F08635-93-C-0020. The work documented in this report was performed from June 1994 to July 1995. The principal investigator, Stewart J. Markgraf is employed by Applied Research Associates Inc. Major Floyd L. Wiseman was the AL/EQS project manager.

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SECTION I

INTRODUCTION

A. OBJECTIVE

This project's objective was to determine the atmospheric fate of trifluoroiodomethane (CF_3I). CF_3I has been proposed as a suitable substitute for certain fire-suppressing halons, most notably Halon 1301 (CF_3Br). In particular, this effort includes studies on the photolysis rates for CF_3I for a variety of sunlight conditions, and the second-order rate for the reaction between CF_3I with the hydroxyl radical ($OH^{\cdot}$), which is present virtually everywhere in the troposphere during daylight hours. These two reactions are likely the only major decay mechanisms for CF_3I in the troposphere. Other reactions, including those with pollutants such as NOx, ozone and hydrocarbons, are likely to make only minor contributions to the atmospheric fate of CF_3I. In addition a short study on the stability of CF_3I in containers, by itself, and in blends is also presented.

B. BACKGROUND

As a result of the 1990 Clean Air Act Amendments and the Montreal Protocol and its amendments, the military, commercial airlines, and chemical manufacturers are attempting to find suitable replacements for Halon 1301 (CF_3Br). CF_3I, because it is chemically and physically similar to other halons, and because it is chemically labile, has been considered to be a promising substitute for replacing halons currently used in unoccupied space total flooding applications and streaming applications. Alone, CF_3I is as effective as Halon 1301, while weighing only a fraction more. It also possesses a low ozone depletion potential (ODP) and low global-warming potential (GWP) due to its short atmospheric lifetime. However, it is precluded from use in occupied spaces due to its toxicity. The lowest observable adverse effect level (LOAEL) for CF_3I is 0.4% concentration (a 5% concentration is needed to put out fires). In this effort, degradation by photolysis was noted and sunlight photolysis studies were performed in the summer, winter and early spring. An $OH^{\cdot}$ radical rate constant study was attempted, but the results were inconclusive. A product study also yielded inconclusive results. A stability study of CF3I in blends and by itself while in storage was also conducted.

C. SCOPE

The work reported here represents only a portion of the information which is required to replace a chemical in the Air Force inventory. In addition to having information on the environmental impact of a new chemical, information is also needed on such things as the cost of implementation (which may include major engineering design changes to the recipient hardware), cost of material production, operational suitability and effectiveness, and toxicity, both human and environmental.

CF_3I, while quite effective in extinguishing fires, is toxic, limiting its application. Even though CF_3I may be suitable only for limited applications, the information contained in this report should be useful for identifying other potential halon replacements for future study. In particular, the data obtained in this effort will probably serve as a good indication of the chemical and physical behavior of compounds structurally similar to CF_3I, but having higher molecular masses. The heavier homologues of CF_3I may be as effective in extinguishing fires, but still reactive enough to be destroyed in the troposphere, and, at the same time, less toxic to humans and the environment than CF_3I.

SECTION II

BACKGROUND

A. Atmospheric Implications of CF_3I

CF_3I is an attractive choice as a halon replacement because of its low ozone-depleting potential and low global-warming potential. It is also effective in fighting fires, requiring only 1.1 times that of Halon-1301 and fitting in approximately the same space. The chemical reactivity of CF_3I can be attributed primarily to the weak C-I bond, which has a bond strength of 218 $kJ \cdot mol^{-1}$. Therefore, during daylight hours, the following process would be expected to occur, at least to some extent, in the troposphere:

$$CF_3I + h\upsilon \longrightarrow CF_3^{\cdot} + I^{\cdot} \qquad (1)$$

Of particular importance is the fate of the atomic iodine radical ($I^{\cdot}$). If the iodine reaches the stratosphere, it will likely contribute to ozone depletion by the same type of destructive chain reaction (shown below) which occurs with chlorine and bromine.

$$C\text{-}X + h\upsilon\,(uv) \longrightarrow C^{\cdot} + X^{\cdot} \qquad (2)$$

$$X^{\cdot} + O_3 \longrightarrow X\text{-}O + O_2 \qquad (3)$$

$$X\text{-}O + O_3 \longrightarrow X^{\cdot} + 2O_2 \qquad (4)$$

X represents $Cl^{\cdot}$, $Br^{\cdot}$, or $I^{\cdot}$, and $C^{\cdot}$ represents the remaining molecular fragment (most often an organic or inorganic carbon-containing fragment). Rather intense ultraviolet (uv) radiation in the range, 290 - 350 nm, enters the stratosphere, and is primarily responsible for cleaving the C-X bonds. Whether iodine enters the stratosphere in atomic or molecular form is irrelevant, since organic bonds to iodine are weak, and will rapidly break once the species enters the stratosphere.

Most of the CF_3I should decompose photolytically or chemically in the troposphere. Of the two fragments resulting from photolysis (Reaction 1), the $CF_3^{\cdot}$ fragment is of little concern regarding ozone depleting potential. The $CF_3^{\cdot}$ will oxidize, forming stable compounds containing C-F and C=O bonds

(The fate of $CF_3^{\cdot}$ is discussed further in Section V). If any oxidation product did reach the stratosphere, it would not be photolyzed because of the very strong C-F and C=O bonds (the bond strengths are 484 and 743 $kJ \cdot mol^{-1}$).

Atomic iodine, however, could conceivably be a problem. If atomic iodine forms a compound which is not readily washed out in the troposphere, it may have a chance to reach the stratosphere. Atomic iodine is relatively soft, and will not likely undergo displacement reactions to any significant degree with many of the species typically present in the troposphere, with the notable exceptions of ozone, nitrogen trioxide and HO_2 (reactions shown below) [1].

$$I^{\cdot} + NO_3 \longrightarrow IO^{\cdot} + NO_2 \qquad (5)$$

$$I^{\cdot} + NO_3 + M \longrightarrow IONO_2 + M \qquad (6)$$

$$I^{\cdot} + O_3 \longrightarrow IO^{\cdot} + O_2 \qquad (7)$$

$$I^{\cdot} + HO_2 \longrightarrow HI + O_2 \qquad (8)$$

These reactions may be the primary means for scavenging atomic iodine in the troposphere. The reaction with ozone would be particularly prolific in polluted urban environments, where ozone is typically at much higher concentrations. HI as well as $IONO_2$ can be taken up by water efficiently and be rapidly scavenged from the atmosphere. The $IO^{\cdot}$ radical can undergo a myriad of reactions, particularly with various urban pollutants, such as NOx, $HO_2^{\cdot}$, ozone, and hydrocarbons. Atomic iodine can also undergo addition reactions with radicals present in the troposphere, such as the reaction with hydroxyl:

$$I^{\cdot} + OH^{\cdot} \longrightarrow IOH \qquad (9)$$

Hydroxyl radicals, which are responsible for the chief degradation mechanism of many urban pollutants, are formed in the presence of sunlight and ozone according to the following scheme:

$$O_3 + h\upsilon \longrightarrow O_2 + O^{\cdot}(^1D) \qquad (10)$$

$$O^{\cdot}(^1D) + H_2O \longrightarrow 2OH^{\cdot} \qquad (11)$$

IOH, as well as the various products formed from the reactions of $IO^{\cdot}$ with urban pollutants, will most likely be washed out by rainfall or scrubbed by aerosols, and hence not contribute to stratospheric ozone depletion.

CF_3I can also react with the hydroxyl radical:

$$CF_3I + OH^{\cdot} \longrightarrow IOH + CF_3^{\cdot} \qquad (12)$$

It is likely that this reaction is not as significant as photoloysis. Part of the purpose of this work is to determine the relative importance between Reactions (1) and (12).

Both photolysis and reaction with the hydroxyl radical are strictly daylight mechanisms, $O^{\cdot}(^1D)$ will not form at night, hence, neither will $OH^{\cdot}$. However, as mentioned above, NO_3 is present at night, and serves as a readily available oxidizing agent for nighttime tropospheric chemistry. Hence, the following reaction may be a significant sink for CF_3I at night:

$$CF_3I + NO_3 \longrightarrow CF_3^{\cdot} + IO^{\cdot} + NO_2 \qquad (13)$$

Even if Reaction (7) is not important, and there is no other significant sink for CF_3I at night, the time required for significant dispersion into the stratosphere is much longer than the diurnal cycle, precluding any major infiltration of CF_3I into the stratosphere.

B. Stability

During the course of the hydroxyl radical experiments in this work, it was noted that CF_3I reacted with certain chloro- and fluorobenzenes even in the absence of light. Similar reactions have been found in the literature [2]. These reactions may pose a problem for long term storage of CF_3I blends since storage of fire fighting appratus and chemicals is not necessarily ideal. Thermal shock from being stored in sunlight or poorly ventiliated areas may start reactions either between CF_3I and the container or between CF_3I and a blending agent. This could lower the effectiveness of CF_3I or its blends for fighting fires and may even produce toxic by-products.

SECTION III

EXPERIMENTAL

A. Experimental Background

The kinetic rate equation for Reaction (12) can be cast as:

$$d[CF_3I]/dt = -k[CF_3I][OH^{\cdot}] \qquad (14)$$

in which k is the second-order rate constant. In the laboratory work reported here, the hydroxyl radicals have been generated by injecting methyl nitrite (CH_3ONO) and nitrogen oxide (NO) into the atmospheric reaction chamber. The pursuant reactions are:

$$CH_3ONO + h\upsilon\ (>300\ nm) \longrightarrow CH_3O^{\cdot} + NO \qquad (15)$$

$$CH_3O^{\cdot} + O_2 \longrightarrow CH_2O + HO_2^{\cdot} \qquad (16)$$

$$HO_2^{\cdot} + NO \longrightarrow OH^{\cdot} + NO_2 \qquad (17)$$

To determine the hydroxyl radical rate constants in the laboratory, the relative rate method [3-6] has been selected. This method is based upon the condition that the reaction of the compound with the hydroxyl radical is the only reaction occuring within the chamber and the concentration of the hydroxyl radical is in excess. This condition reduces the overall order of the reaction to one. Hence, the integrated rate equation is simply:

$$\ln[CF_3I]_t/[CF_3I]_0 = -k't \qquad (18)$$

in which the subscripts refer to time = t and time = 0 respectively, and k' is $k[OH^{\cdot}]$ in Equation (14). A reference compound whose OH rate constant is already known is injected into the chamber along with the CF_3I. Assuming that reaction with the hydroxyl is the only significant reaction of the sample compound and the reference compound, it is straightforward to show that:

$$\ln[S]_0/[S]_t = k_s/k_r \ln[R]_0/[R]_t \qquad (19)$$

in which [S] and [R] refer to sample and reference, respectively, and k_s and k_r are the pseudo-first-order rate constants for the hydroxyl reactions with the sample and the reference, respectively. Since the hydroxyl radical concentration, which is difficult to estimate in chamber experiments, cancels out in the ratio, k_s/k_r, the use of Equation (19) is made possible. Furthermore, the application of Equation (19) is experimentally straightforward. A plot of $\ln[S]_0/[S]_t$ against $\ln[R]_0/[R]_t$ should yield a straight line with a slope equal to k_s/k_r and a zero intercept. The degree of linearity of the plot and proximity of the intercept to zero serve as good indicators of the quality of the experimental data or of the appropriateness of the assumptions.

Products resulting from the reactions of the hydroxyl radical and the sample may also be analyzed by this analytical method, except now the reference compound is absent. Product concentration may be determined by simple calibration and percentage of product formation may be determined. This method of product analysis, is more complicated if the product undergoes any appreciable secondary reactions. In this case, the product concentration will not follow a simple first-order rate law.

The other degradation mechanism, photolysis, given by Reaction (1), may also be treated as a first-order process, except that the rate constant is now a function of meteorological parameters such as the time of day, degree of cloud cover, and the angle of the sun. Equation (18) can be used to analyze data from photolytic studies, so long as other potential chemical and physical processes do not interfere.

Since the photolytic lifetime of a species is influenced by meteorological parameters, it is useful to be able to generate an empirical algorithm which casts the rate constant as functions of the appropriate meteorological parameters. However, the meteorological parameters are in actuality secondary parameters. The primary parameter, to which all the others depend, is the absorption cross-section (visible and ultraviolet regions) of the species in question. To determine this, a sample is placed into a gas cell at various pressures and the absorbances at the various maxima (if more than one exists) are measured. A variation of the Beer-Lambert law (given below) is used to determine the absorption coefficient at the absorbance maxima.

$$A = \varepsilon b l \tag{20}$$

where A is the absorbance, ε is the molar absorption coefficient, b is the partial pressure (in torr) of the species in question, and l is the pathlength in centimeters. The absorption cross section (symbolized by σ, in units of $cm^2 \cdot molecule^{-1}$) is obtained by multiplying the molar absorption coefficient, which is wavelength dependent, by the conversion factor, 7.11×10^{-17} $torr \cdot cm^3 \cdot molecule^{-1}$. The range of values for the absorption cross section can then be used to calculate the photolytic rate constant, k_p, according to the following summation:

$$k_p = \sum_{290\,nm}^{\lambda} \sigma(\lambda)\, \phi(\lambda)\, J(\lambda) \qquad (21)$$

in which $\sigma(\lambda)$ is the absorption cross section, $\phi(\lambda)$ is the primary quantum yield, and $J(\lambda)$ is the actinic flux. The summation begins at the ultraviolet cutoff region in the troposphere, and goes to the longest appropriate wavelength for the absorbing species in question.

Heat can also break a chemical down. While this is generally not a problem under ordinary circumstances, in storage however, extremes can be reached. Large tanks can be stored outside in sunlight or in poorly ventilated areas and as a result, the walls of the tank can get quite warm. CF3I has been shown to react on several metal surfaces [7] [8] [9], of special note nickel [10] [11], a substance used in stainless steel. Stainless steel is used in several storage applications, including fire fighting apparatus. Breakdown products can include: IF, CF_2; with blends: HI, HF; and others, some of which are corrosive and toxic. This of special concern since these fire fighting compounds would be expected to stay stable until needed, which may be years. A test of stability would be to place the compounds into the expected storage container and simulate some ranges of heating that could be expected for long periods of time. This should focus on the temperature of the walls as it is likely that reactions would occur there.

B. Chemicals and Equipment

CF_3I was obtained from both PCR scientific (97% pure) and Aldrich (99%) and was used without further purification. Methyl was synthesized (12) in-house by reacting methyl alcohol with sodium nitrite. Sulfuric acid was added dropwise onto a mixture of the alcohol and sodium nitrite. The organic nitrite was swept away by a stream of nitrogen into a cold finger immersed in a methanol slush bath at -60°C. The compound was stored in a commercial lecture bottle at room temperature until needed. The NO (99%) was obtained from Matheson and used without further purification. The chemicals used as reference compounds for the hydroxyl radical reaction studies were either on hand or ordered from Aldrich, Fisher, PCR, or Malinkdroct at 99% purity and used without further purification. Reference compounds were as follows: 2-Ethoxyethylacetate, Fluorobenzene, Nitrobenzene, Nitroethane, Nitromethane (Aldrich); Ethane, Propane (Malinkdrot); Chlorobenzene, 1,2-Dichloroethane, 1,1,1-trichloroethane Pentafluoroethane, 1,2,4-trichlorobenzene (Fisher); fluoroethane, 1,1,1,2,3,3,3-heptafluoropropane (PCR). Chemicals used in the stability study (CF3I, FM-200, HFC-236fa) were prepackaged from USAF Wright laboratories at unknown purity.

The following equipment was used for the rate studies and product analysis. Heat sealed Teflon bags ranging from 30- to 75-L capacity with stainless steel fittings were made and cleaned by photolyzing with NO at least three times. A light tight box, lined with reflective foil, was lighted with seven Q-panel uv-340, two Q-panel uv-351, one GE F40bl and six Phillips TL-40W/03 lamps to simulate sunlight. The chamber had the temperature held constant by a air blower and was connected to the GC through a Teflon sampling line and a 1.5-ml sampling loop. A 3000-L Teflon bag was also used for the product study. The product study used a Hewlett-Packard gas chromatograph (GC), model # 5890, utilizing a Fourier transform infrared (FTIR) spectrometer and mass spectrometer (MS) in parallel as detectors. The columns used for the product studies were a 30-m GS-Q (0.53 mm ID) linked with a 30-m RTx-502.2 (0.53 mm ID) using the following temperature program: 5 minutes @ 32°C, 7°C/minute to 150°C for 12 minutes. The photolysis and OH radical rate studies also used a Hewlett-Packard 5890 GC with an electron capture detector (ECD) and a flame ionization detector (FID) in parallel. Two sets of GC columns were used for the studies. The first set was linked in the following order: a 30-m GS-Q (0.53 mm ID) with a 30-m RTx-502.2 (0.53 mm ID); using this temperature program: 5 minutes @ 32°C, 7°C/minute to 150°C for 12 minutes. This was used for the non-polar references and some sunlight photolysis studies. Also used was this setup: a 30-m RTx-200 (0.53 mm ID); a 30-m RTx-502.2 (0.53 mm ID); a 15-m SPB-2330 (0.32 mm ID); and a 30-m RTx-2330

(0.25 mm ID), linked together in the order as listed. The temperature program was: 14 minutes @ 30°C, 10°C/minute to 120°C for 7 minutes (increase to 250°C for 35 minutes for high boiling-point compounds). This linkage setup was used for polar references and most sunlight photolysis studies.

The cross-section studies were performed with a Cary 3E uv-vis spectrophotometer using a 100-mm x 22-mm borosilicate glass gas cell sealed at the ends with quartz windows. A vacuum manifold capable of achieving <0.05 torr was used to manipulate the pressure in the gas cell.

The stability study utilized an Hewlett-packard GC/MS with this cloumn steup: a 30-m GS-Q (0.53 mm ID) with a 30-m RTx-502.2 (0.53 mm ID); using this temperature program: 5 minutes @ 32°C, 7°C/minute to 150°C for 12 minutes. A "Blue M" oven with a thermometer was used for heating.

C. Procedure

The sunlight study was carried out by injecting varying amounts of CF_3I into a Teflon bag which was then filled with air. Final concentrations varied from 0.05 part per million (ppm) to two ppm. The bag was then placed into the light-tight chamber and allowed to equilibrate for approximately 30 minutes. Samples were analyzed using a GC with an ECD detector to determine a baseline, then the bag was secured upon an easel and taken outside and exposed to sunlight. The bag was then brought back inside and placed into the chamber for sampling purposes by the GC-ECD at various times during the day, and then returned outside. Temperature and cloud cover were also monitored when sampling occurred. These experiments were conducted on the following dates: August 31, 1994; January 9,11,25, February 1,9, and March 14, 1995 under various weather conditions.

The hydroxyl studies were attempted by the relative rate method employed by Roger Atkinson (5,6). A reference compound was selected, with a reaction rate similar to that of the compound of interest. The compounds were mixed together in the Teflon bag and placed into the light-tight chamber. Methyl nitrite (used to generate the hydroxyl radicals) and NO (used to suppress ozone production) were then added and a baseline was established by GC-ECD. The mixture was then photolyzed for varying amounts of time in the chamber, and the changes in concentration were monitored by gas chromatography. Various problems, discussed later, led to the conclusion that the relative rate technique as applied here was unsuitable for measuring the rate constant for the reaction of hydroxyl with CF_3I. Possibly the flash discharge technique with fluorescence detection might prove successful for this particular reaction.

A simple mathematical treatment to estimate the rate constant was also attempted. This procedure uses a free energy relationship involving bond dissociation energies to estimate the rate constant. Similar procedures have been investigated by J.S. Gaffney (13) and further investigated by Maria Tosato (14). This treatment used the logarithms of the bond dissociation energies for CF_3Br, CF_4, CF_3Cl, and CF_3H, and graphically compared them to their respective rate constants. A regression analysis was performed on the data to obtain a best-fit line. The rate constant for CF_3I was then estimated from the equation of the line using the bond dissociation energy for CF_3I.

The product studies from the hydroxyl radical reactions and photolysis alone were done by two variations of the methodology described for the hydroxyl radical study. CF_3I was injected into the 3000-L atmospheric chamber, along with NO and methyl nitrite to produce the hydroxyl radicals and ensure minimization of ozone formation. The mixture was then photolyzed at various intervals. The other variation was to inject only CF_3I into a Teflon bag and photolyze for hours. Both methods were analyzed on the GC-MS-FTIR system with the GS-Q column setup described above.

For the uv cross-section, the Cary 3E uv-vis spectrometer was programmed to read from 190 nm to 900 nm with a single pass at 500 nm per minute. The bandwidth was 0.2 nm. The gas cell was evacuated to <0.05 torr, and CF_3I was introduced at the following pressures to analyze the cross-section; 1.57, 1.96, 2.96, 3.94, 6.56, 9.87, 15.4, 21.1, 26.3, and 39.8 torr. The following additional pressures: 106, 241.1, 352.6, 401.5, and 760 torr were used to determine if other electronic transitions were present that could influence the photolysis rate.

For the stability study, the chemicals came prepackaged in stainless steel containers with Nupro™ valves. Initial chromatograms and mass spectra were obtained and the containers were placed into the oven at 150°F for 3 days and additional readings were made. Then the containers were returned to the oven and the oven temperature increased to 200°F and left overnight. Further readings were made and the containers were returned to the 200°F for 2 days and final reading were taken.

SECTION IV

RESULTS

A. Photolytic Studies

The resulting data from the photolytic studies followed an exponential decay curve with time. The data sets, given in the appendix, ranged from four days to 78 days. The first-order rate constants ranged form 1.72 day^{-1} to 3.07 $hour^{-1}$, depending upon the cloud cover (light cloud cover in the summer to heavy clouds in the winter). Detailed data is shown in Table 1. As clouds moved in during a testing period, that day's data sets showed significant scatter, commensurate with the variation in cloud cover. Since Teflon absorbs uv radiation to a small extent in the region of interest, as illustrated in the appendix, the results do have an error factor inherent in them, artificially adding time to the degradation of CF_3I.

B. UV-Vis Studies

The data from the uv studies is given in Table 2. CF_3I was observed to have a broad, featureless absorbance band with a maximum at 267 nm. The pressures employed were in the range of 1.65 torr to 39.8 torr. A graphical comparison of absorbance to pressure gave a correlation coefficient of 0.998 and the resulting slope was used in determining the cross-section. This yielded a cross section of 4.16×10^{-19} $cm^2 \cdot molecule^{-1}$ with ± 1.5% error in the slope. This is in poor comparison to Susan Solomon's number of 6.45 [1]. This discrepancy may be due to poor performance of the spectrophotometer or the pressure measuring equipment. At higher pressures (up to 760 torr), no other electronic transitions were observed.

Table 1. Comparison of Photolysis for Various Degrees of Cloud Cover and for Seasons

Day of Year	Lifetime in days 10 hours sunlight/day	Cloud coverage
8/31/94	4.3	light to clear
1/9/95	19.6	light to moderate
1/9/95	53.8	heavy
1/11/95	45.1	heavy
1/25/95	19.4	light overcast
1/25/95	78	very heavy (85%)
1/25/95	51.2	overall
2/1/95	8.4	light
2/9/95	8.9	light to moderate
2/9/95	12.3	moderate
2/9/95	17.5	overall
3/14/95	20.2	light to moderate

Table 2. Uv-vis Cross-section of CF_3I

Pressure torr	Concentration molecule·cm^{-3}	Absorbance	Wavelength nm	Cross-section cm^{2}·molecule^{-1}
1.65	5.09 E+16	0.1596	266	6.88 E-19
2.04	6.35 E+16	0.182	266	6.34 E-19
3.04	9.59 E+16	0.254	266	5.94 E-19
4.02	1.27 E+17	0.3146	267	5.56 E-19
6.64	2.13 E+17	0.4856	266	5.20 E-19
9.95	3.2 E+17	0.6947	267	4.96 E-19
15.4	4.99 E+17	1.0309	267	4.76 E-19
21.1	6.84 E+17	1.3658	267	4.6 E-19
26.3	8.52 E+17	1.3381	267	3.62 E-19
39.8	1.29 E+18	2.3844	267	4.26 E-19

C. Hydroxyl Rate Studies

The hydroxyl rate experiments yielded little useful results for several reasons. First, it was impossible to conduct the hydroxyl studies without some interference from photolysis. The C-I bond in CF_3I is so easily broken, that even radiation from room lights can rupture the bond. In addition, the iodine radical appeared to be reacting with the many of the reference compounds, particularly the halogenated benzenes, such as fluorobenzene, causing other unidentified reactions. Many of the more appropriate reference compounds were either sensitive to the room light, or unstable in the reaction chamber or in the GC detectors. Nitro compounds, while being sensitive on the ECD, proved to be too unstable in the bag under experimental conditions and at the temperatures present in the GC. Chlorofluorocarbons and chlorocarbons were sensitive enough on the ECD, but had no sensitivity on the FID. Additional undesirable side reactions, which continued beyond the initiation time, were caused by the chlorine radical which was produced by the chamber light. One reference compound, 1,2,4-trichlorobenzene, did not even require initiation in order to react. Fluorocarbon compounds, the initial choice for these studies, showed a remarkable lack of sensitivity on both ECD and FID, making them quite unsuitable for analysis (the target response level is around 5 ppm, but the fluorocarbons showed responses only at 100 to 1000 ppm). Alcohols, low molecular weight alkanes and amines suffered similar problems. Higher Molecular weight alkanes, alkynes, alkenes, ethers, other amines, and diols reacted too rapidly to be of use in the analysis. The target rate constant is around 10^{-14} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ [15], which is the expected rate constant for CF_3I, but the rate constants for these compounds are usually around 10^{-12} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$. Moreover, the hydroxyl precursors, methyl and ethyl nitrite, seemed to react fast enough with the hydroxyl to be competitive with CF_3I. Other techniques for generating the hydroxyl radical (for instance, photolysis of H_2O_2 and photolysis of ozone and water) were attempted, but failed due to water interfering on the GC.

D. Product Studies

Unfortunately, no useful results were obtained from the product studies either. The analysis on the GC-FTIR-MS system showed very little, if any, of the products which would likely be formed by photolysis or hydroxyl radical reaction. The inability to isolate and identify an iodine containing product may have been due to a surface interaction of iodine with the Teflon bags, similar to that of bromine with Teflon (16). Further literature searches revealed that the predicted intermediate products of the $CF_3^{\cdot}$ radical are unstable in the presence of water [17-22] (which was present as a component of the air in the bags), and quickly break down into simpler products such as HF and NO, both of which were present from the beginning of the test.

E. Free energy calculations

Use of the free energy relationship between bond strength and hydroxyl rates was hampered by a lack of good data for the hydroxyl rate constants of structurally similar molecules (literature rate constants for many of the target compounds are only approximate values). Table 3 contains the bond dissociation energies (BDE)[23] and hydroxyl rate constants for several compounds structurally similar to CF_3I [24] (the bond dissociation energy for CF_3I is also included). Figure 1 shows a plot of the logarithm of the rate constant as a function of the bond dissociation energy. The correlation coefficient (R^2) for the line is quite poor, indicating that this is a questionable means of estimating the rate constant, at least for this case. The predicted rate constant for the reaction of CF_3I with hydroxyl using this method is on the order of 10^{-16} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$. In comparison with literature values for similar compounds, this number appears to be too small by nearly two orders of magnitude.

F. Stability Studies.

The stability studies gave somewhat inconclusive results. The GC/MS showed no products forming and the ratios of the peaks appeared to behave in a low level, random fashion, indicating no change or insignificant change. However an acid gas was detected after the first 200°F test and in subsequent tests for the CF_3I bottle and the CF_3I and FM-200 blend, indicating a possible change. The valve on the CF_3I and HFC-236fa bottle failed during the first 200°F test leading to incomplete results. Further testing is definitely indicated.

Table 3. Pertinent kinetic and thermodynamic data for estimating the hydroxyl rate constant for CF_3I

Compound	Rate constant $cm^3 \cdot molecule^{-1} \cdot s^{-1}$	Bond	BDE $cal \cdot mole^{-1}$	Log[OH˙]
CF_3Br	1.0E-16	C-Br	71	-16
CF_4	4.0e-16	C-F	130	-15.40
CF_3Cl	7.0e-16	C-Cl	86	-15.15
CF_3H	2.40E-16	C-H	106	-15.62
CF_3I	-------	C-I	56	-----

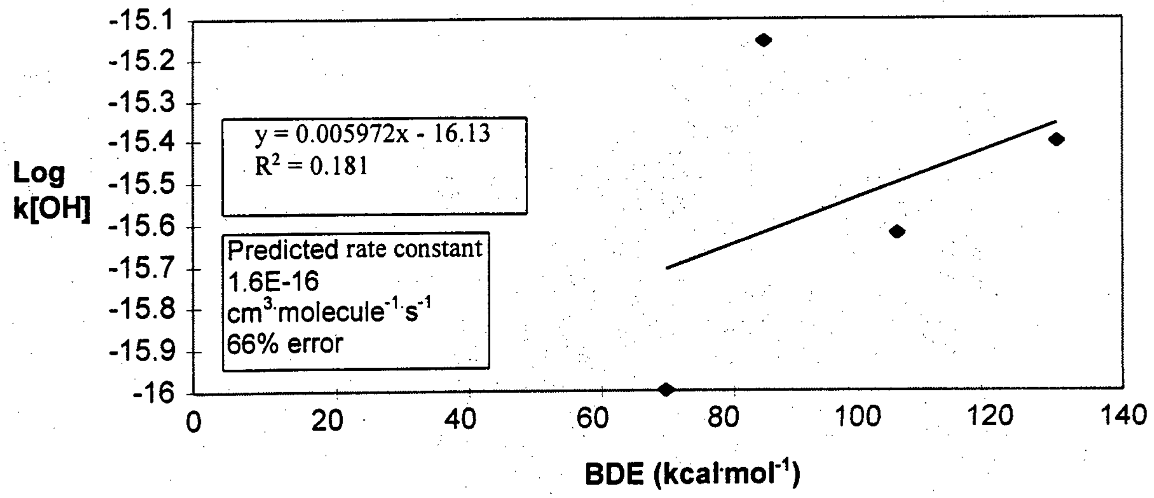

Figure 1. Predicted rate constant for reaction of $OH^{\cdot}$ with CF_3I

SECTION V

DISCUSSION AND RECOMMENDATIONS

A. Discussion

The prime mechanism for CF_3I degradation is photolysis. CF_3I has a broad featureless absorption from 225 to 300 nm with a peak at 267 nm. Susan Solomon (1) of the National Oceanic and Atmospheric Administration (NOAA) at Boulder, CO measured the uv cross section and found it to be 6.45×10^{-19} $cm^2 \cdot molecule^{-1}$ at 296 K. With this data, she computed an overall lifetime for CF_3I of two days (assuming clear skies), a surface albedo of 0.30, and a quantum efficiency of one. The uv cross section measured in this study is 4.16×10^{-19} $cm^2 \cdot molecule^{-1}$, in rather poor agreement with Solomon. Since further uv analysis revealed no other electronic transitions at other wavelengths or pressures, it was concluded that there are no other photolysis effects over the range studied, other than the one at 267 nm. The data resulting from the photolysis experiments in this study indicates a wide variability in lifetimes, due predominantly to cloud cover. For instance, on a partly cloudy sky, the lifetime, defined as 99.9% disappearance, was 19 hours, but dramatically increased to 78 hours when the heavier clouds moved in later in that day. The angle of the sun, while important over the course of the day, did not appear to show as much of an effect over the course of the seasons (a sunny day in both winter and summer had half-lives that differed only by a few hours).

Atmospheric removal of CF_3I by the reaction with the hydroxyl radical is only a secondary process. This reaction is appears to be orders of magnitude slower than photolysis. A study performed by Brown (15) of Oxford, UK in 1989 gave an hydroxyl rate constant of 3.1×10^{-14} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ (which corresponds to a lifetime of 256 days). A previous study was done in 1979 (25) and gave a value of 1.2×10^{-13}, but questions about the validity of this earlier work makes this value suspect, hence, the Brown number is the one accepted. Studies in this work were unable to yield good numbers for the rate constant, due to the problems discussed earlier.

Predicted products for CF_3I should be the same for the hydroxyl reaction as for the photolysis, since the $CF_3^{\cdot}$ radical is formed in either case. The radical reacts with oxygen to form

CF_3O_2, which in turn reacts with NO to form CF_3O. These reactions are quite rapid, with rate constants on the order of 10^{-11} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ (17). CF_3O then reacts with water or methane to form CF_3OH, or with NO again to form COF_2 and FNO. The $CF_3^{\cdot}$ radical will also react with other hydrocarbons in a polluted atmosphere to form CF_3OH and a hydrocarbon radical (18,19). The $CF_3O^{\cdot}$ radical has been studied and shown to have little, if any impact on stratospheric ozone (20). COF_2 is a strong irritant and is very quickly hydrolyzed by water according to the Merck index (21). FNO is also a strong irritant, but has industrial uses in rocket oxidizers, fluorinating agents, and stabilizing liquid SO_3. It further breaks down in the presence of water to form nitric acid, HF, and NO (21). The eventual fate of atomic iodine is not well known, although, as mentioned earlier, it probably forms compounds which are easily scrubbed in the troposphere. Soloman (1) indicated through several reactions that iodine would have a lifetime of only a few weeks. As already shown in the Background Section, it forms IOH, HI, $IONO_2$ or possibly $IO^{\cdot}$ if in the presence of sufficient ozone (as would likely be the case for photolysis of CF_3I in an urban atmosphere). Since the I-O bond is weak, IOH probably breaks down in reactions with organic compounds. Depending on the local weather conditions and altitude release, the formation of atomic iodine or $IO^{\cdot}$, which is a short-lived radical, may participate in lower stratospheric ozone destruction (1). Atomic iodine and $IO^{\cdot}$ can also react with organic peroxy radicals in a polluted urban airshed to form a variety of products (22). IOH, HI and $IONO_2$ are rapidly hydrolyzed by water and are removed.

The stability of CF_3I and blends with other halocarbons may be somewhat problematic. During the course of the hydroxyl radical experiments in this work, it was noted that CF_3I continued reacting with certain chloro- and fluorocarbons after the lights were turned off, in one case light was not even needed to start the reaction. Similar reactions have been found in the literature as well as reactions on metal surfaces. These reactions may pose a problem for long term storage of CF_3I blends. Short-term tests using CF_3I, alone or blended with FM-200 or HFC-236fa in stainless steel bottles at elevated temperatures (150°F to 200°F for three to four days) suggested no detectable change. However, due to the acid gas formation, long term storage of blends containing CF_3I is still inadvisable based upon the results of this work. Further testing is indicated.

B. Recommendations

For lower tropospheric use, CF_3I appears to be an environmentally friendly compound. It has a low ODP (0.008) and a low GWP (1.0), due principally to its short atmospheric lifetime from photolysis. It primarily forms a variety of irritants as it breaks down. These irritants in turn break down quickly to form substances such as nitric acid, HF, and NO. Polluted atmospheres will generate more complex reactions involving CF_3I, and studies using simulated urban atmospheres will need to be conducted in order to gain a better understanding of the total environmental impact of using CF_3I. Its toxicity definitely warrants caution in its use, and limits its use strictly to unoccupied spaces and in some streaming agent applications. CF_3I appears to be stable in short term storage, but probably not in long term storage. In upper tropospheric use and above, CF_3I takes on a decidedly environmentally unfriendly posture due to the reactions of atomic iodine. Atomic iodine is at least as effective as atomic bromine in ozone destruction, and may actually be more detrimental [26]. This could lead to significant ozone destruction, even with small releases of CF_3I in or near the stratosphere.

For ground-based uses and uses in aircraft not traveling near or above the tropopause (from two to eight kilometers, depending upon location), and taking into consideration toxicity, storage, and weather effects, CF_3I may be a suitable substitute for Halon-1301. CF_3I may not be a suitable substitute for Halon-1301 in aircraft traveling at or above the tropopause.

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Sunlight Data

Sunlight Photolysis for: CF_3I
Half-life calculations
date: 1-9-95

Cumulative Sunlight Time (min)	$[CF_3I]$ ppm	ave. $[CF_3I]$ ppm	$-\mathrm{Ln}\frac{[CF_3I]}{[CF_3I]_o}$	Temp Celcius	Cloud Cover %	Cloud Type	Comments
0							
0	0.2201						
0	0.2215	0.2208	0	-11.6	25	Cirrostratus	Cloud types extrapolated from notes. Sun angle about 45 degrees for most of the day.
66	0.209		0.0580	-11.1	15	Cirrus	
111	0.207		0.0677	-5.5	<10	Cirrostratus	
172	0.195		0.1274	-5.3	<10	Cirrostratus	
239	0.191		0.1449	-2.8	<10	Cirrostratus	
289	0.186		0.1715	-1.1	<10	Altostratus	
348	0.178		0.2154	-0.5	18	Altostratus	not used
396	0.179		0.2098	-1.9	85	Stratus	not used
461	0.174		0.2382	-6.4	85	Stratus	

Regression Output:

Constant	0.0092
Std Err of Y Est	0.0110
R Squared	0.9815
No. of Observations	7
Degrees of Freedom	5
X Coefficient(s)	0.0005
Std Err of Coef.	3.6E-05

1/e Lifetime = 28 hours

The half-life of CF_3I during 1-9-95 is:

under

1.18E+03 minutes
1.96E+01 hours
8.18E-01 days
1.17E-01 weeks
2.69E-02 months
2.24E-03 years

The expected lifetime (99.9% disappearance) of CF3I assuming constant sunlight 24 hrs. a day these conditions

1.17E+04 minutes
1.96E+02 hours
8.16E+00 days
1.17E+00 weeks
2.68E-01 months
2.23E-02 years

Sunlight Photolysis for: CF_3I
Half-life calculations
date: 1-9-95

Cumulative Sunlight Time (min)	$[CF_3I]$ ppm	ave. $[CF_3I]$ ppm	$-\mathrm{Ln}\frac{[CF_3I]}{[CF_3I]_o}$	Temp Celcius	Cloud Cover %	Cloud Type	Comments
0	0.178	0.178	0	-0.5	18	Altostratus	Sun angle drops from 45 degrees to <15 degrees. This data is from the late afternoon set.
48	0.179		-0.0056	-1.9	85	Status	
113	0.174		0.0227	-6.4	85	Status	

Regression Output:

Constant	-0.0058
Std Err of Y Est	0.0124
R Squared	0.6578
No. of Observations	3
Degrees of Freedom	1
X Coefficient(s)	0.0002
Std Err of Coef.	0.0001

The half-life of CF_3I during 1-9-95 is:

3.23E+03 minutes
5.38E+01 hours
2.24E+00 days
3.20E-01 weeks
7.37E-02 months
6.14E-03 years

1/e Lifetime = 3.23 days

The expected lifetime (99.9% disappearance) of CF_3I assuming constant sunlight 24 hrs. a day under these conditions

3.22E+04 minutes
5.36E+02 hours
2.24E+01 days
3.19E+00 weeks
7.35E-01 months
6.12E-02 years

Sunlight Photolysis for: CF_3I
Half-life calculations
date: 1-25-95

Cumulative Sunlight Time (min)	$[CF_3I]$ ppm	ave. $[CF_3I]$ ppm	$-\mathrm{Ln}\frac{[CF_3I]}{[CF_3I]_o}$	Temp Celcius	Cloud Cover %	Cloud Type	Comments
0	1.002						Continuous sunlight shining through cloud cover. No temperature measurements taken.
0	0.993						
0	0.988	0.994	0		85	Cirrus	
160	0.922		0.0691		85	Cirrus	
223	0.947		0.0423		85	Cirrus	
240	0.963		0.0256		35	Cirrus	
276	0.941		0.0551		15	Cirrus	
308	0.921		0.0766		15	Cirrus	
351	0.902		0.0974		15	Cirrus	

Regression Output:

Constant	0.0021
Std Err of Y Est	0.0217
R Squared	0.6332
No. of Observations	7
Degrees of Freedom	5
X Coefficient(s)	0.0002
Std Err of Coef.	7.68E-05

1/e Lifetime = 3.07 days

The half-life of CF_3I during 1-25-95 is:

3.07E+03	minutes
5.12E+01	hours
2.13E+00	days
3.05E-01	weeks
7.01E-02	months
5.84E-03	years

The expected lifetime (99.9% disappearance) of CF_3I assuming constant sunlight 24 hrs. a day under these conditions

3.06E+04	minutes
5.10E+02	hours
2.13E+01	days
3.04E+00	weeks
6.99E-01	months
5.82E-02	years

Sunlight Photolysis for: CF_3I
Half-life calculations
date: 1-25-95

Cumulative Sunlight Time (min)	$[CF_3I]$ ppm	ave. $[CF_3I]$ ppm	$-\ln\frac{[CF_3I]}{[CF_3I]_o}$	Temp Celcius	Cloud Cover %	Cloud Type	Comments
							This data set uses the data from later in the day when the light but continuous cloud cover broke up. No temperature recorded.
0	0.963	0.963	0		35	Cirrus	
36	0.941		0.0231		15	Cirrus	
68	0.921		0.0445		15	Cirrus	
111	0.902		0.0654		15	Cirrus	

Regression Output:

Constant	0.0013
Std Err of Y Est	0.0025
R Squared	0.9943
No. of Observations	4
Degrees of Freedom	2
X Coefficient(s)	0.0005
Std Err of Coef.	3.18E-05

1/e Lifetime = 28 hours

The half-life of CF_3I during 1-25-95 is:

1.17E+03	minutes
1.94E+01	hours
8.10E-01	days
1.16E-01	weeks
2.66E-02	months
2.22E-03	years

The expected lifetime (99.9% disappearance) of CF_3I assuming constant sunlight 24 hrs. a day under these conditions

1.16E+04	minutes
1.94E+02	hours
8.07E+00	days
1.15E+00	weeks
2.65E-01	months
2.21E-02	years

Sunlight Photolysis for: CF_3I
Half-life calculations
date: 1-25-95

Cumulative Sunlight Time (min)	$[CF_3I]$ ppm	ave. $[CF_3I]$ ppm	$-\mathrm{Ln}\frac{[CF_3I]}{[CF_3I]_o}$	Temp Celcius	Cloud Cover %	Cloud Type
0	1.002					
0	0.993					
0	0.988	0.9943	0		85	Cirrus
160	0.922		0.0691		85	Cirrus
223	0.947		0.0423		85	Cirrus
240	0.963		0.0256		35	Cirrus

Comments

Continuous sunlight shining through cloud cover. No temperature measurements taken.

Regression Output:

Constant	0.0112
Std Err of Y Est	0.0295
R Squared	0.3096
No. of Observations	4
Degrees of Freedom	2
X Coefficient(s)	0.0001
Std Err of Coef.	0.0001

1/e Lifetime = 4.7 days

The half-life of CF_3I during 1-25-95 is:

4.69E+03 minutes
7.82E+01 hours
3.26E+00 days
4.65E-01 weeks
1.07E-01 months
8.92E-03 years

The expected lifetime (99.9% disappearance) of CF_3I assuming constant sunlight 24 hrs. a day under these conditions

4.68E+04 minutes
7.79E+02 hours
3.25E+01 days
4.64E+00 weeks
1.07E+00 months
8.89E-02 years

Sunlight Photolysis for: CF_3I
Half-life calculations
date: 2-1-95

Cumulative Sunlight Time (min)	$[CF_3I]$ ppm	ave. $[CF_3I]$ ppm	$-\mathrm{Ln}\frac{[CF_3I]}{[CF_3I]_o}$	Temp Celcius	Cloud Cover %	Cloud Type	Comments
0	0.93						Sun angle from 35 degrees to 50 degrees.
0	0.935						
0	0.929	0.9313	0	11	25	Cirrocumulu	
56	0.898		0.0339	14	25	Cirrocumulu	
128	0.866		0.0702	17	<10	Cirrus	
198	0.697		0.2873	17	<10	Cirrus	

Regression Output:

Constant	-0.0326
Std Err of Y Est	0.0663
R Squared	0.8252
No. of Observations	4
Degrees of Freedom	2
X Coefficient(s)	0.0013
Std Err of Coef.	0.0004

1/e Lifetime = 12.2 hours

The half-life of CF_3I during 2-1-95 is:

5.07E+02	minutes
8.45E+00	hours
3.52E+01	days
5.03E-02	weeks
1.16E-02	months
9.65E-04	years

The expected lifetime (99.9% disappearance) of CF_3I assuming constant sunlight 24 hrs. a day under these conditions

5.05E+03	minutes
8.42E+01	hours
3.51E+00	days
5.01E-01	weeks
1.15E-01	months
9.62E-03	years

Sunlight Photolysis for: CF_3I
Half-life calculations
date: 2-9-95

Cumulative Sunlight Time (min)	$[CF_3I]$ ppm	ave. $[CF_3I]$ ppm	$-\ln\frac{[CF_3I]}{[CF_3I]_o}$	Temp Celcius	Cloud Cover %	Cloud Type	Comments
							Sun angle from 40 degrees to 55 degrees back to 42.
0	1.157						
0	1.034	1.0955	0	0.6	<10	Cirrus	
90	1.2		-0.1488	8	<10	Cirrus	
147	1.129		-0.0878	10	<10	Cirrus	
221	1.09		-0.0527	12	20	Altocumulus	
287	0.914		0.1811	8.5	65	Stratocumulus	
372	0.953		0.1393	7.5	100	Stratocumulus	

Regression Output:

Constant	-0.1172
Std Err of Y Est	0.1063
R Squared	0.4663
No. of Observations	6
Degrees of Freedom	4
X Coefficient(s)	0.0006
Std Err of Coef.	0.0003

1/e Lifetime = 25.3 hours

The half-life of CF_3I during 2-9-95 is:

1.05E+03 minutes
1.76E+01 hours
7.32E-01 days
1.05E-01 weeks
2.41E-02 months
2.00E-03 years

The expected lifetime (99.9% disappearance) of CF_3I assuming constant sunlight 24 hrs. a day under these conditions

1.04E+04 minutes
1.75E+02 hours
7.29E+00 days
1.04E+00 weeks
2.40E-01 months
2.00E-02 years

Sunlight Photolysis for: CF_3I
Half-life calculations
date: 2-9-95

Cumulative Sunlight Time (min)	$[CF_3I]$ ppm	ave. $[CF_3I]$ ppm	$-\ln\frac{[CF_3I]}{[CF_3I]_o}$	Temp Celcius	Cloud Cover %	Cloud Type	Comments
							Sun angle from 40 degrees to 55 degrees back to 42.
0	1.2	1.2	0	8	<10	Cirrus	
57	1.129		0.0609	10	<10	Cirrus	not used
131	1.09		0.0961	12	20	Altocumulus	
197	0.914		0.2722	8.5	65	Stratocumulus	
282	0.953		0.2304	7.5	100	Stratocumulus	

Regression Output:

Constant	-0.0158
Std Err of Y Est	0.0482
R Squared	0.8863
No. of Observations	4
Degrees of Freedom	2
X Coefficient(s)	0.00128
Std Err of Coef.	0.00032

1/e Lifetime = 3.23 days

The half-life of CF_3I during 2-9-95 is:

3.23E+03	minutes
5.38E+01	hours
2.24E+00	days
3.20E-01	weeks
7.37E-02	months
6.14E-03	years

The expected lifetime (99.9% disappearance) of CF_3I assuming constant sunlight 24 hrs. a day under these conditions

3.22E+04	minutes
5.36E+02	hours
2.24E+01	days
3.19E+00	weeks
7.35E-01	months
6.12E-02	years

Sunlight Photolysis for: CF_3I
Half-life calculations
date: 3-14-95

Cumulative Sunlight Time (min)	$[CF_3I]$ ppm	ave. $[CF_3I]$ ppm	$-\text{Ln}\frac{[CF_3I]}{[CF_3I]_o}$	Temp Celcius	Cloud Cover %	Cloud Type	Comments
0	1.98	1.98	0	21	15	Cirrostratus/ Altostratus	Sun @ 39
48	2		-0.0100	23	22.5	Cirrostratus/ Altostratus	Sun @ 50 Cloud den.inc overcast
81	2		-0.0100	22.5	80	Stratus/ Stratocumulus	
120	1.92		0.0307	24	50	Stratocumulus/ Cirrostratus	Sun @ 53-55 patchy cumulus
156	1.86		0.0625	24.5	75	Stratocumulus/ Cirrostratus	Sun @ 60 Sc conjestus 90 + %
227	1.74		0.1292	28	50	Stratocumulus/ Cirrostratus	Sun @ 62
275	1.7		0.1524	25	75	Stratocumulus/ Cirrostratus	Turreted & patchy clouds
340	1.64		0.1884	22.5	100(15)	Altostratus/ (Stratocumulus)	Sun @ 52, shining thru
397	1.62		0.2006	23	95(10)	Cirrostratus/ (Altocumulus)	Sun @ 45 Shine thru Cs
435	1.63		0.1945	22.5	95(25)	Cirrostratus/ (Altocumulus)	Sun @ 35 shine thru Cs

Regression Output:

Constant	-0.0244
Std Err of Y Est	0.0227
R Squared	0.9411
No. of Observations	10
Degrees of Freedom	8
X Coefficient(s)	0.0005
Std Err of Coef.	5.03E-05

1/e Lifetime = 12.2 days

The half-life of CF_3I during 3-14-95 is:

1.22E+03	minutes
2.03E+01	hours
8.46E-01	days
1.21E-01	weeks
2.78E-02	months
2.32E-03	years

The expected lifetime (99.9% disappearance) of CF_3I assuming constant sunlight 24 hrs. a day under these conditions

1.21E+04	minutes
2.02E+02	hours
8.43E+00	days
1.20E+00	weeks
2.77E-01	months
2.31E-02	years

Sunlight Photolysis for: CF_3I
Half-life calculations
date: 1-11-95

Cumulative Sunlight Time (min)	$[CF_3I]$ ppm	ave. $[CF_3I]$ ppm	$-\mathrm{Ln}\frac{[CF_3I]}{[CF_3I]_o}$	Temp Celcius	Cloud Cover %	Cloud Type
0	0.6246					
0	0.6372	0.6309	0	13.5	100	Fog
60	0.614		0.0370	17.5	100	Fog
114	0.607		0.0485	19	40	Stratus
211	0.59		0.0769	NA	40	Stratus
273	0.582		0.0806	NA	40	Stratus
310	0.576		0.0910	NA	40	Stratus
403	0.564		0.1120	NA	40	Stratus

Comments

Thermometer broke, daily high around 21 degrees celcius. Solar angle varied from 20 to close to 50 to degrees. Sun vis as a disk throug cloudy all day.

NA - not available

Regression Output:

Constant	0.0139
Std Err of Y Est	0.0089
R Squared	0.9526
No. of Observations	7
Degrees of Freedom	5
X Coefficient(s)	0.0002
Std Err of Coef.	2.54E-05

1/e Lifetime = 2.73 days

The half-life of CF_3I during 1-11-95 is:

2.72E+03 minutes
4.54E+01 hours
1.89E+00 days
2.70E-01 weeks
6.21E-02 months

The expected lifetime (99.9% disappearance) of CF_3I assuming constant sunlight 24 hrs. a day under these conditions

2.71E+04 minutes
4.52E+02 hours
1.88E+01 days
2.69E+00 weeks
6.19E-01 months

5.18E-03 years

5.16E-02 years

Sunlight Photolysis for: CF_3I
Half-life calculations
date: 8-31-95

Cumulative Sunlight Time (min)	$[CF_3I]$ ppm	ave. $[CF_3I]$ ppm	$-\ln\frac{[CF_3I]}{[CF_3I]_o}$	Temp Celcius	Cloud Cover %	Cloud Type
0	0.0517		0	21	25	Cumulus
60	0.0483		0.0680	23	25	Cumulus
214	0.0326		0.4611	29	<10	Cumulus
338	0.0213		0.8867	32	25	Cumulus

Comments

Temperatures are extrapolated from recorded highs and lows from Bay county water plant.

Regression Output:

Constant	-0.0522
Std Err of Y Est	0.0670
R Squared	0.9821
No. of Observations	4
Degrees of Freedom	2
X Coefficient(s)	0.0026
Std Err of Coef.	0.0002

1/e lifetime = 6.3 hours

The half-life of CF_3I during 8-31-95 is:

2.61E+03	minutes
4.35E+00	hours
1.81E-01	days
2.59E-02	weeks
5.96E-03	months
4.97E-04	years

The expected lifetime (99.9% disappearance) of CF_3I assuming constant sunlight 24 hrs. a day under these conditions

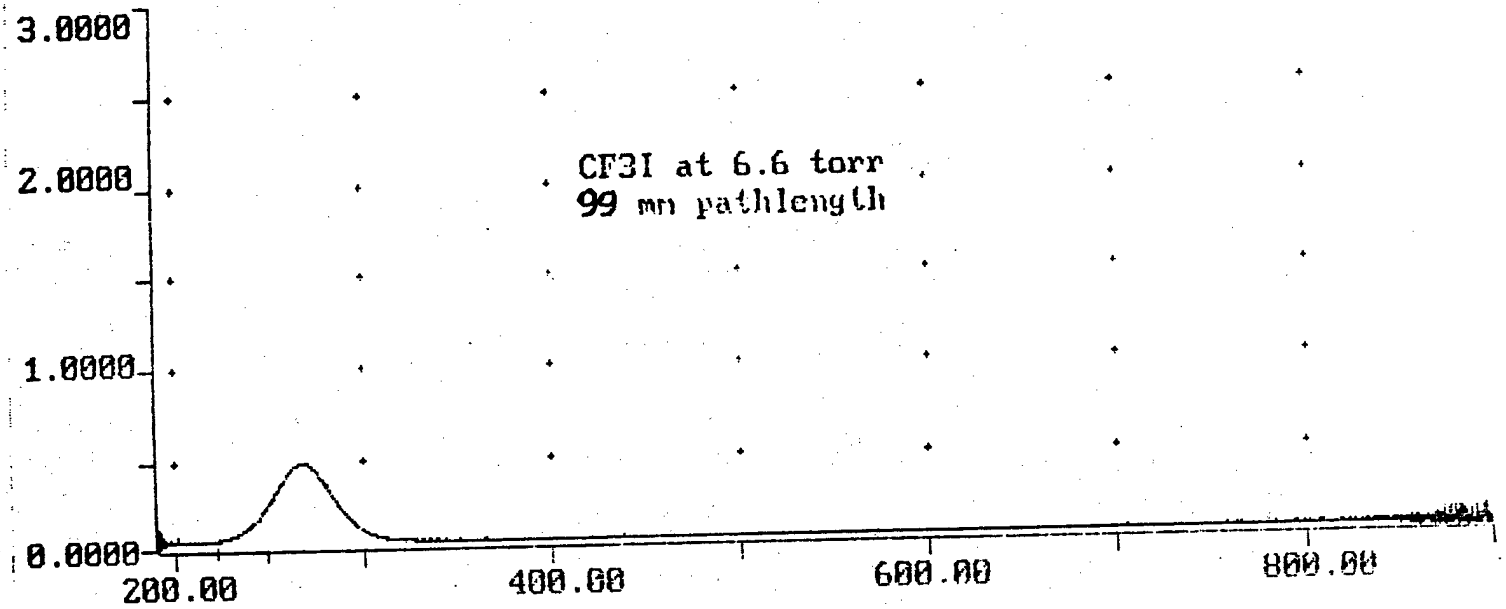
2.60E+03	minutes
4.34E+01	hours
1.81E+00	days
2.58E-01	weeks
5.94E-02	months
4.95E-03	years

Example of UV-Vis Data
Uv-Vis Chart

0.0659	CF3I-cross			4 Apr 1995	**900.00**
	Gain	255	SBW	0.5	
ABS	Baseline	ON	Page	3	NM

Press F2 to EDIT

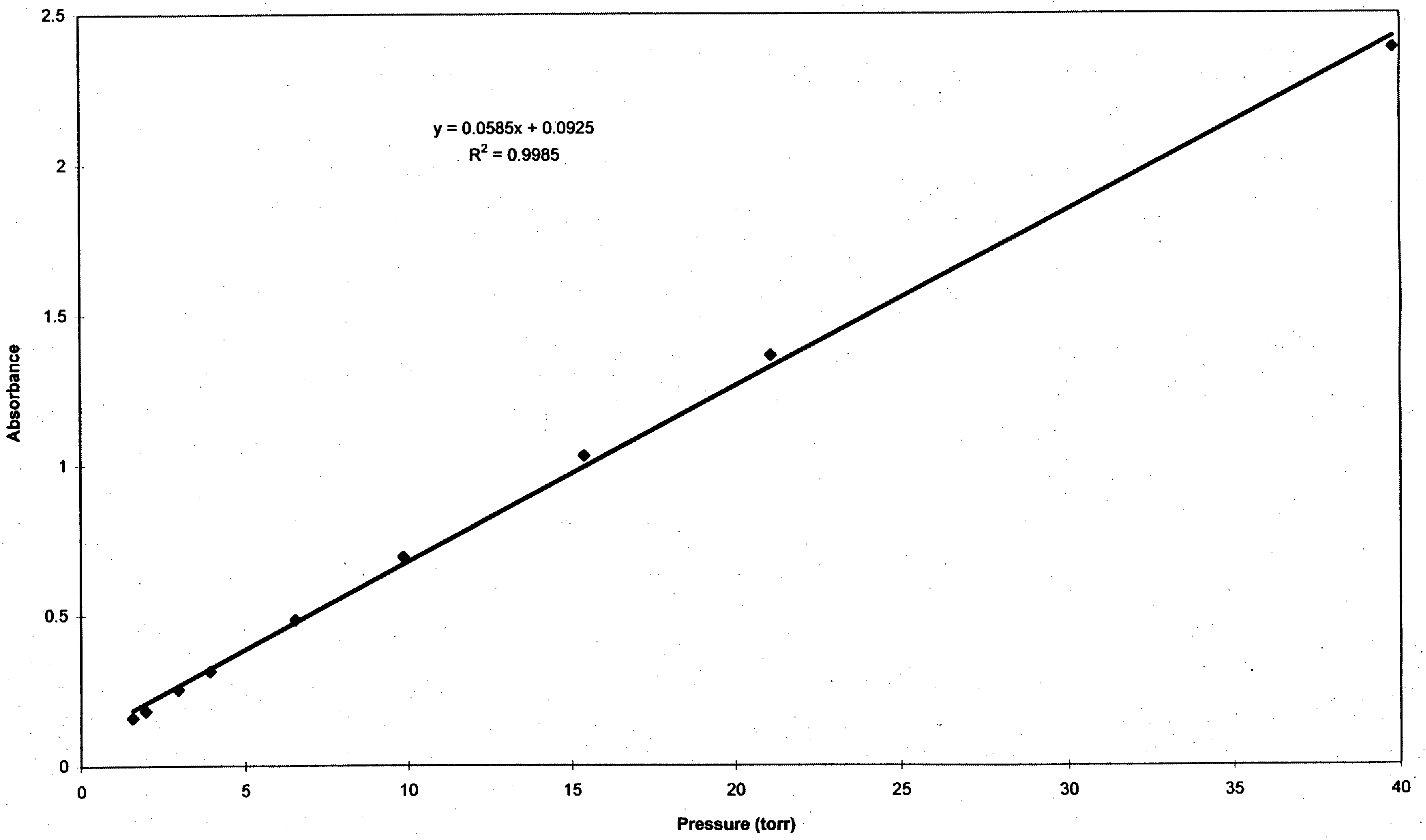
DISPLAY DATA



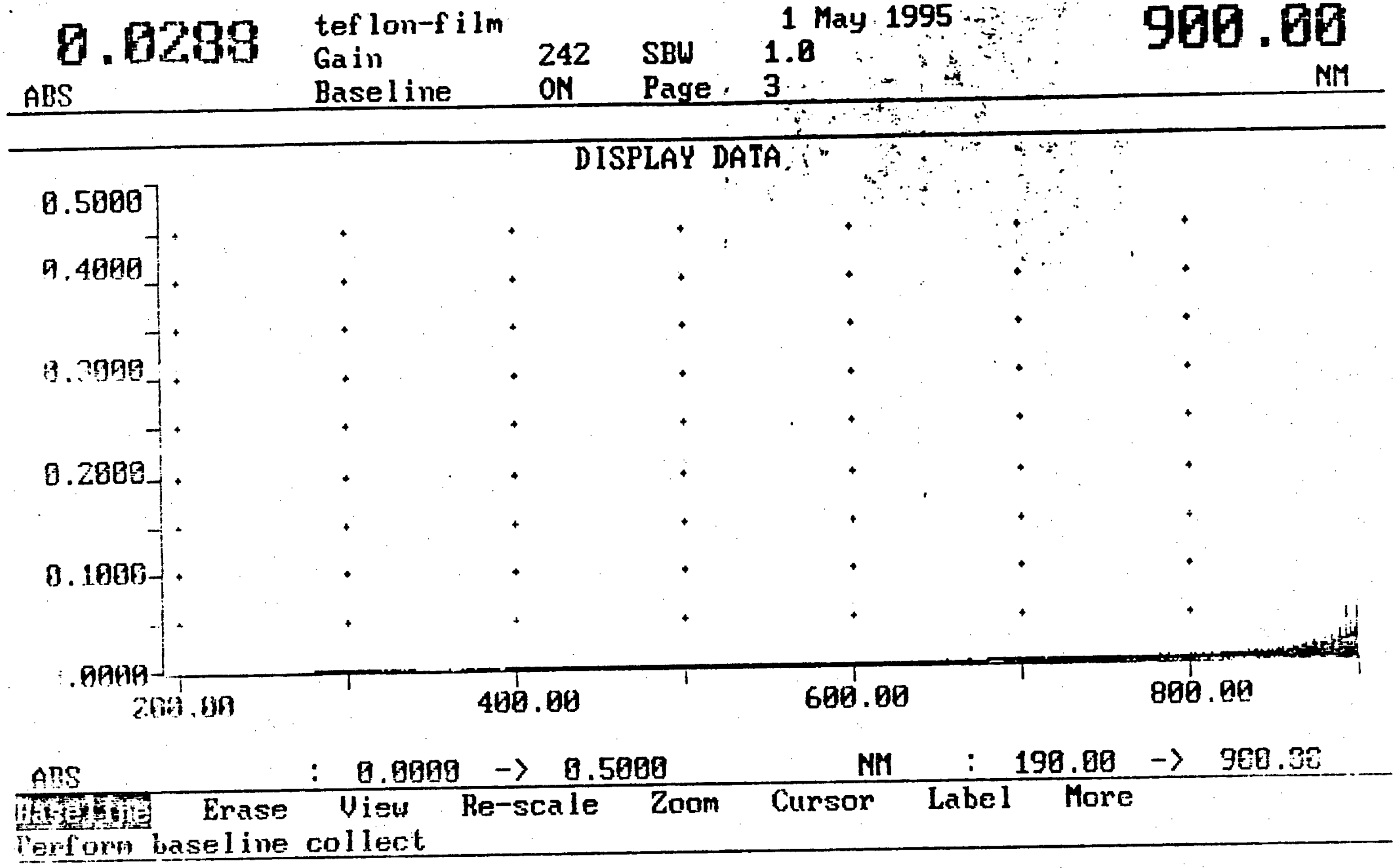
CF3I at 6.6 torr
99 mm pathlength

ABS : 0.0000 -> 3.0000 NM : 190.00 -> 900.00

Pressure vs. UV-Vis absorbance



Teflon Film Absorbance



0.0288 ABS

teflon-film

Gain 242 SBW 1.0

Baseline ON Page 3

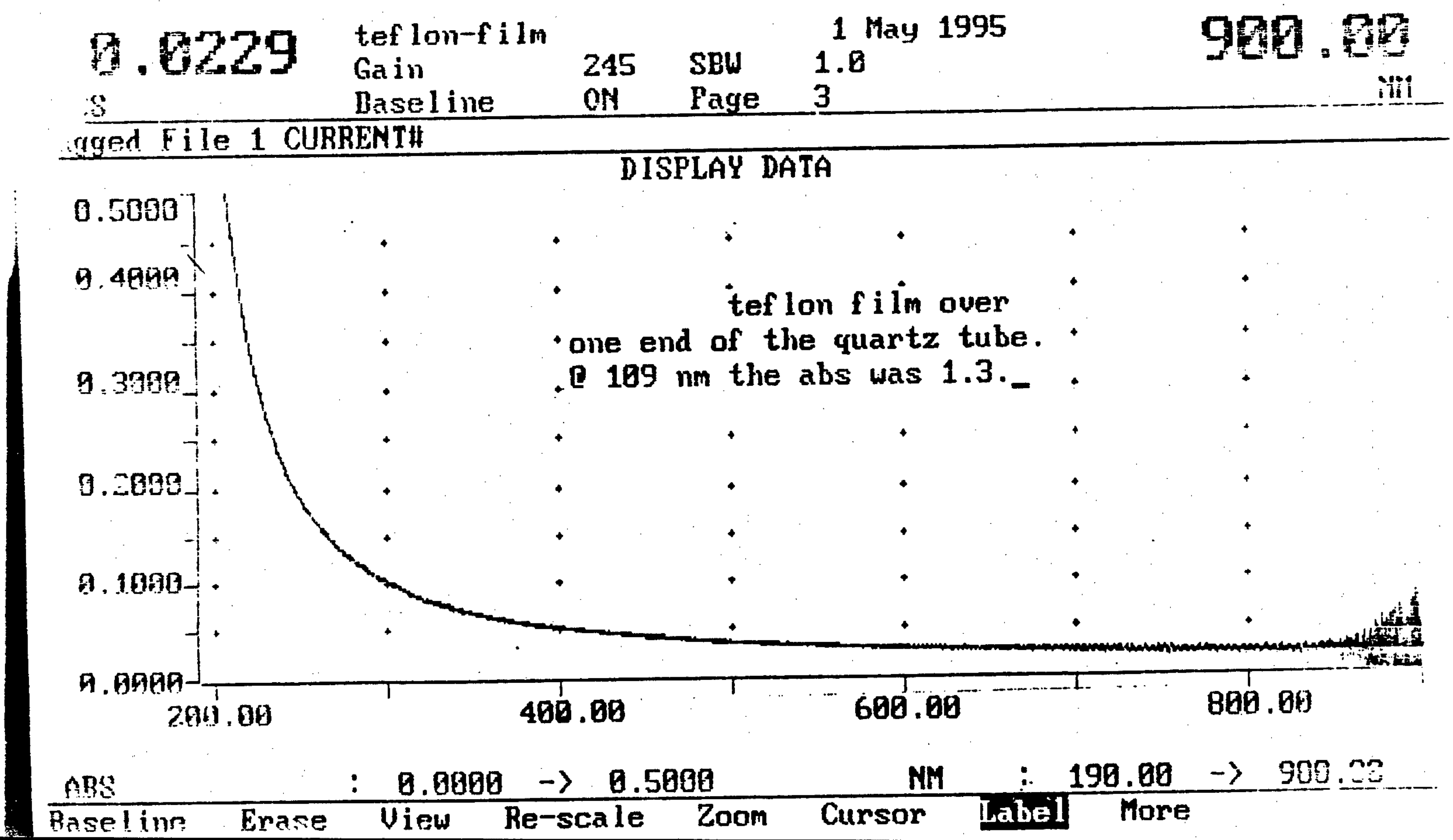
1 May 1995

900.00 NM

DISPLAY DATA

ABS : 0.0000 -> 0.5000 NM : 190.00 -> 900.00

Perform baseline collect



0.0229 S

teflon-film

Gain 245 SBW 1.0

Baseline ON Page 3

1 May 1995

900.00 NM

gged File 1 CURRENT#

DISPLAY DATA

teflon film over
one end of the quartz tube.
@ 109 nm the abs was 1.3._

ABS : 0.0000 -> 0.5000 NM : 190.00 -> 900.00