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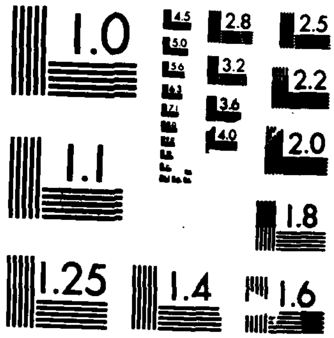

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# Kevlar Photochemical Degradation Mechanisms

by
Madeline S. Toy, Ph.D.
Science Applications International Corp.
for the
Aerosystems Department

APRIL 1987

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The objective of this program was to investigate and determine Kevlar's photochemical degradation mechanisms, rate constants, and activation energies in air. The underlying reason was to understand the oxidative photodegradation processes, which would help to provide service life forecast under the sunlight conditions and to aid effective method development against its photodecomposition.

The first significant accomplishment of the project was the new and novel analytical approach, which demonstrated the rate constant and activation energy determinations of Kevlar's photooxidative processes. The 0.2 atm of oxygen-18-labeled environment in a solar chamber simulates the air exposure under sunlight conditions. The technique also allows the radial $^{18}$O-distribution measurement from the fiber surface toward the fiber center. The data from the accelerated experimental conditions in the solar chamber in an $^{18}O_2$-atmosphere are differentiated from the similar ambient daylight exposure effects.

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mechanisms, oxidative photodegradation process, photooxidative degradation, tensile strength, tensile modulus, breaking strain, moisture region, critical oxygen index, chemical resistance, light wavelength, polymer degradation, energy level, absorption spectrum, ultraviolet, aromatic amides, benzanilide, amide bonds, oxygen molecules, peroxide intermediates, carboxylic acid, nitroso compounds, infrared spectroscopy, potentiometric titration, anionic polyelectrolyte, dialkylamide-LiCl, cationic polyelectrolyte, lithium cation-amide, dialkylamide solvent, N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), crystalline solvates, polymer solutes, anisotropic, photolysis chamber, Pyrex conical pipe, quartz sleeve, $^1$HNMR, deuterated, vacuo, Nicolet spectrometer, decarboxylation, gas chromatography, GC-mass spectrometer, $^{13}$CNMR, macromolecule, reactant, radial distribution.

19. ABSTRACT (Contd.) Carbon dioxide

The second significant accomplishment was the recognition of a thermal decomposition pattern of Kevlar in concentrated sulfuric acid at 196°C to give the same two types of decarboxylations: one yields one mole of $CO_2$ per $-\!(C_7H_5NO)\!-$ moiety and the other gives two moles of $CO_2$ per $-\!(C_7H_5NO)\!-$ moiety. The half life of the former is 4 to 12 hours and appears to originate from the amide linkages' carbonyl groups. The latter's half life is 660 hours and is from two of the six carbons of its aromatic rings.

The third significant accomplishment was the analytical methodology applied to deduce the four photooxidative processes. The data on the total $CO_2$ evolved from the samples were measured by gas chromatography and the isotopic $CO_2$ ($^{46}CO_2$ and $^{48}CO_2$) data by GC/mass spectroscopy. The rate constants of the two major photooxidative degradation processes at 25°C were deduced from 1/2 $^{18}O_2$ per $-\!(C_7H_5NO)\!-$ (i.e., to produce $^{46}CO_2$ product, $t_{1/2} = 42$ hours) at 196°C and the other from $^{18}O_2$ per $-\!(C_7H_5NO)\!-$ (i.e., to produce $^{48}CO_2$ product, $t_{1/2} = 8$ minutes) at 196°C. The rate constants of the former process was estimated as $1.10 \times 10^{-8}$ l mole$^{-1}$ second$^{-1}$ and the latter as $1.03 \times 10^{-12}$ l mole$^{-1}$ second$^{-1}$. The activation energies of these two processes were deduced as 10.8 kcal/mole for the former and 15.7 kcal/mole for the latter.

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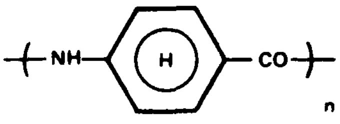
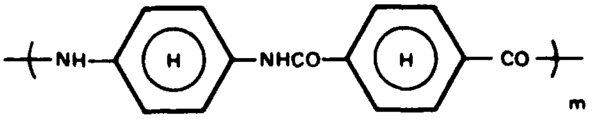
# INTRODUCTION

Kevlar is du Pont's trade name for poly(p-benzamide) and poly(p-phenylene terephthalamide) (II):



I.

and



II.

The Kevlar moiety in this report is addressed as $\left(C_7H_5NO\right)$, because II expressed by its repeating units is $\left(C_{14}H_{10}N_2O_2\right)_m$, which is $\left(C_7H_5NO\right)_{2m}$ to be simplified as $\left(C_7H_5NO\right)_x$, where $x = 2m$. Kevlar belongs to the aramid family of high modulus fiber-forming organic polymers. The aramids are a series of isomeric fully aromatic polyamides that can *withstand service-life stress at high temperature without deformation and degradation* (References 1 and 2). The aramids' inherent flame resistance, high thermal and chemical stablity, and high modulus fulfill a new source for engineering materials.

Kevlar fibers were supplied by du Pont as Kevlar-29 and -49. The former is characterized by high tensile strength and the latter by high initial modulus (Reference 3). Table 1 summarizes some of the properties of Kevlar fibers (Reference 4). Some common Kevlar-29 end uses are in ropes and cables, which are as strong as steel at one-fifth the weight, and in ballistic vests. Some Kevlar-49 end uses are in reinforcing resins and composites for aerospace structures, boat hulls, and sport equipment.

Since many of Kevlar applications such as fabrics, cords, webbings, threads, and cables result in sunlight exposure, which degrades the material, this work aimed to investigate and determine Kevlar's photochemical degradation mechanisms, rate constants, and activation energies in air. The underlying reason was to understand its oxidative photodegradation processes, which can help to provide its service-life forecast under sunlight conditions and to develop an effective method to prevent the photodecomposition.

# THEORETICAL STUDIES

## PHOTODEGRADATIONS

Before certain light wavelength can cause polymer degradation, two conditions must be met: (1) the polymer must absorb at that particular wavelength and (2) the polymer must

TABLE 1. Properties of Kevlar Fibers.

| Property | Value | Units |
|---|---|---|
| Density | 1.45 | $g\ cm^{-3}$ |
| Ultimate tensile strength | 23.3 | $q\ dtex^{-1}$ |
| | 2.76 | GPa |
| Tensile modulus | | |
| (Kevlar-29) | 556 | $q\ dtex^{-1}$ |
| | 62 | GPa |
| (Kevlar-49) | 1166 | $g\ dtex^{-1}$ |
| | 130 | GPa |
| Breaking strain | | |
| (Kevlar-29) | 3.6 | % |
| (Kevlar-49) | 2.1 | % |
| Moisture region | 1.5 | % |
| Continuous use | 240 | C |
| Critical oxygen index | 0.29 | % |
| Chemical resistance[a] | . . . | . . . |

[a] Resistance to organic solvents, fuels, lubricants, strong acids and bases, and hydraulic fluids.

absorb a wavelength of light of sufficient energy level to break their chemical bonds. Figure 1 shows the absorption spectrum of Kevlar and the light spectrum from the sun at the earth's surface (Reference 5). The sensitive wavelengths for the outdoor use of Kevlar are the overlap area of these two curves; that is, the wavelengths between 300 to 450 nanometers (nm).

Although only small amounts of this near ultraviolet and part of the visible light region are present under ordinary fluorescent lamps or in sunlight filtered by windows, the fresh Kevlar yarn with its normal yellow color ordinarily darkens under the exposure. The effect of ultraviolet light varies with the thickness of the Kevlar item exposed. Kevlar is described as self-screening by du Pont, because only the fibers at the surface are subject to photochemical degradation (Reference 6). However, our work herein has provided new evidence by exposing Kevlar fabric in an oxygen-18-labeled atmosphere in a simulated solar chamber. We found that the $^{18}O$-containing Kevlar species were also present at the fiber center above the natural background level.

Aromatic amides (i.e., benzanilide) were reported to photodegrade in the presence of oxygen to give carboxylic acids (e.g., benzoic acid) as the major products (Reference 7). Carlsson, Gan, and Wiles also reported the photodegradation mechanism of poly(p-benzamide) in air by homolytic cleavages of its amide bonds, insertions of oxygen molecules before the radical paired recombinations, and rearrangements of the peroxide intermediates to give carboxylic acid and nitroso end groups. However, the latter formation is based on the presumptive evidence due to the labile nature of the nitroso compounds, which are unlikely to

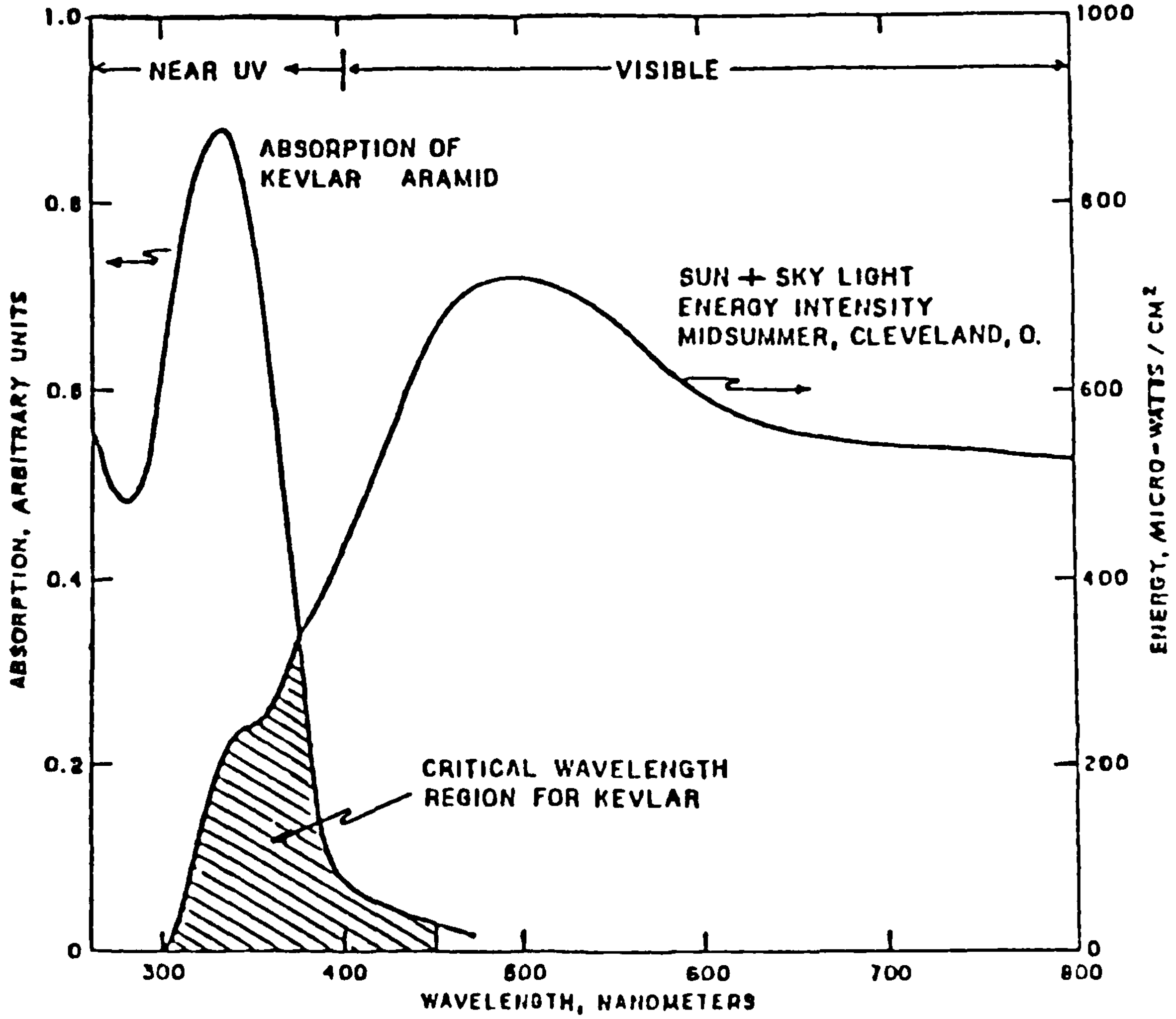


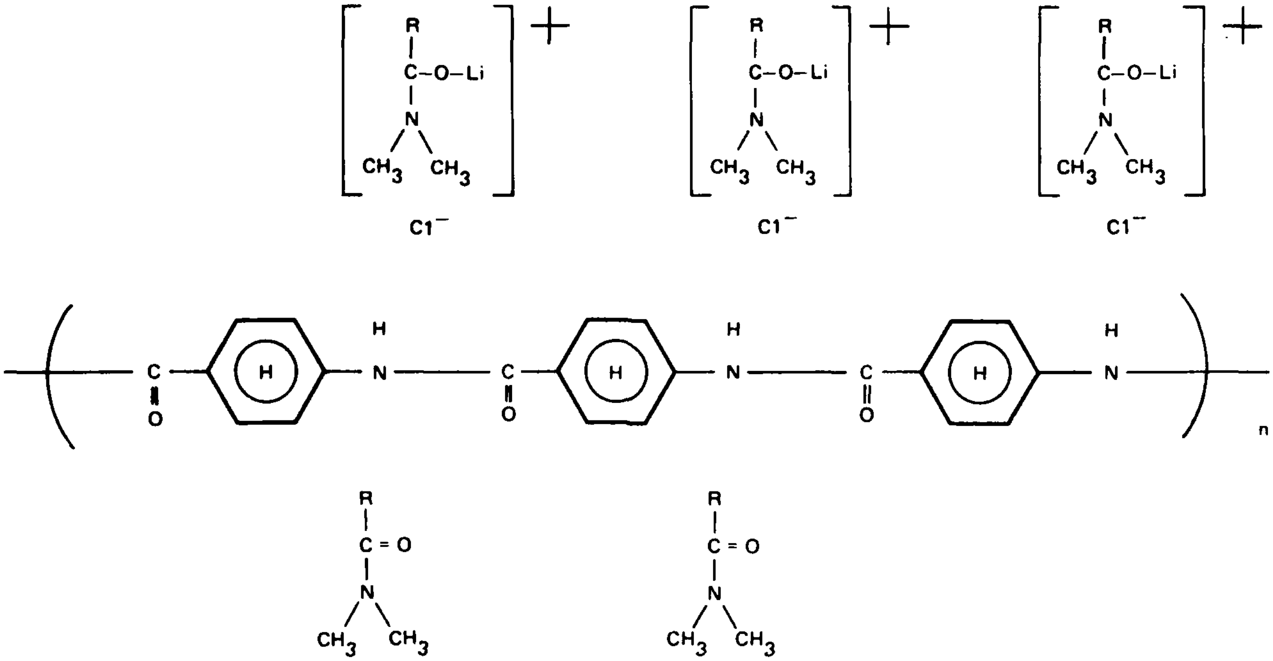
FIGURE 1. Overlap of Absorption of Kevlar With Solar Spectrum.

accumulate during the photooxidative conditions; whereas the carboxylic acids are determined by infrared spectroscopy and potentiometric titration (Reference 8). In other words, after the photooxidative degradation of Kevlar fibers, the oxidized polymeric fragments contain mostly two types of terminal groups, a carboxylic acid end and another labile nitroso end.

## KEVLAR SOLUTION STRUCTURES

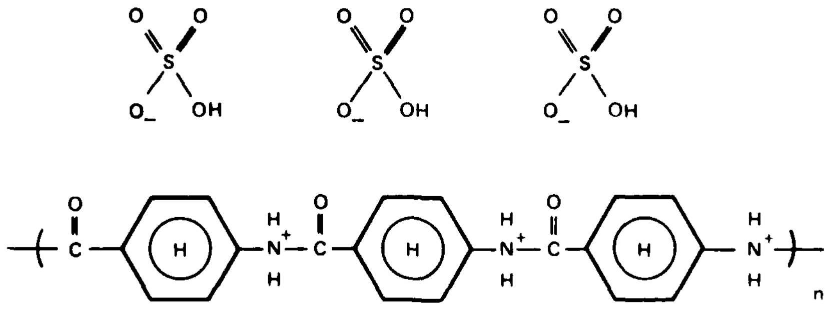
The solution structure of Kevlar has been reported to form anionic polyelectrolyte in dialkylamide-LiCl solutions (Reference 9) and cationic polyelectrolyte in concentrated sulfuric acid (Reference 10). Acccording to Panar and Beste (Reference 9), the N-H groups in dialkylamide-LiCl solutions are associated with chloride anions to form the negatively charged polyelectrolyte, which is solvated by weak positively charged lithium cation-amide complexes.

The neutral entity is then soluble in dialkylamide solvent. The role of dialkylamide solvent [e.g., N,N-dimethylacetamide (DMAc) and N,N-dimethylformamide (DMF)] is shown below:



Where R is $CH_3$ for DMAc and H for DMF.

Gardner states in Reference 10 that the two aramids, poly(p-phenylene terephthalamide) (II) and poly(p-benzamide) (I), form crystalline solvates with sulfuric acid and their amide groups are protonated. The structure consists of hydrogen bonded sheets containing the polymer alternating with sulfuric acid molecules. The sheets are close-packed. The crystalline structure of the oligomer/sulfuric acid complex is suggested below:



The N-H groups are associated with the protons to form the positively charged polyelectrolyte, which is solvated by negatively charged mobile hydrogen sulfate anions.

The solutions of Kevlar derive the crystalline rod-like configuration from their rigid repeating units, bond direction, and solvent association (Reference 11). They are different from the crystalline solutions of poly-($\gamma$-benzyl-L-glutamate), which derives its rod-like character from the helix formation in selected solvents (Reference 12). The extended rigid chain structure of Kevlar polymer solute is produced by the para-linked benzene ring and the partial double bond character of the carbon-nitrogen bond in predominantly the trans amide linkages (Reference 13). The rod-like crystalline (anisotropic) polymer solutes have been reported in the literature as being undetectable by high resolution $^1$HNMR due to their very large intramolecular nuclear dipolar interactions (References 9 and 14). However, in principle, when the rod-like polymer solute is in the degraded state and in high dilution, this problem should disappear or be greatly reduced. We had some success with the photodegraded Kevlar solutions but not without problems (see the section "NMR Studies" later in this report).

## MECHANICAL DESIGN

A simulated solar photolysis chamber (Figure 2) was designed and built to study Kevlar fabric at several temperatures and photolysis times. The photolysis chamber consists of a Pyrex conical pipe outside and a quartz sleeve inside. The top and bottom aluminum annular end plates enclose the area between the Pyrex (7.6 cm id) and quartz (4.5 cm od) tubes into an annular chamber 21.5 cm high with gas inlet and outlet and valves attached. The photolysis chamber's short arc lamp, which is vertically suspended at the center of the quartz sleeve, passes its irradiance through the quartz wall onto the Kevlar-29 fabric in a confined atmosphere (e.g., atmospheric air, oxygen at 0.2 atm, or oxygen-18-labeled gas at 0.2 atm) at specified temperature and time.

A high-pressure ozone-free mercury-xenon arc lamp at 200 watts was purchased from UVP (San Gabriel, Calif.). Its irradiance is estimated at 125 times that of the sun by comparing its spectral power output with the solar spectral irradiance at air mass 2 (Reference 15). A typical air mass 2 (terrestrial at a 30-degree altitude) sun produces 749 W/m$^2$. Thus, an exposure of 1/2 hour is equivalent to 62.5 hours under the sun (at 749 W/m$^2$). The ozone-free bulb cuts off the ultraviolet irradiance below 300 nm for closer resemblance to the solar spectrum.

This apparatus provides the means to investigate Kevlar's photochemical degradation rate constants, activation energies, and mechanisms in air. For atmospheric air runs, the presence of some ozone is anticipated, since oxygen generates ozone under photolytic conditions (References 16 through 18).

It was found essential to remove the surface lubricants (about 1 to 3% by weight) from the as-received Kevlar-29 fabric by using a solvent extraction method prior to the solar exposure tests (see section entitled "Experimental"). These lubricants interfered with the photodegradation processes and the sample analyses (Reference 15).

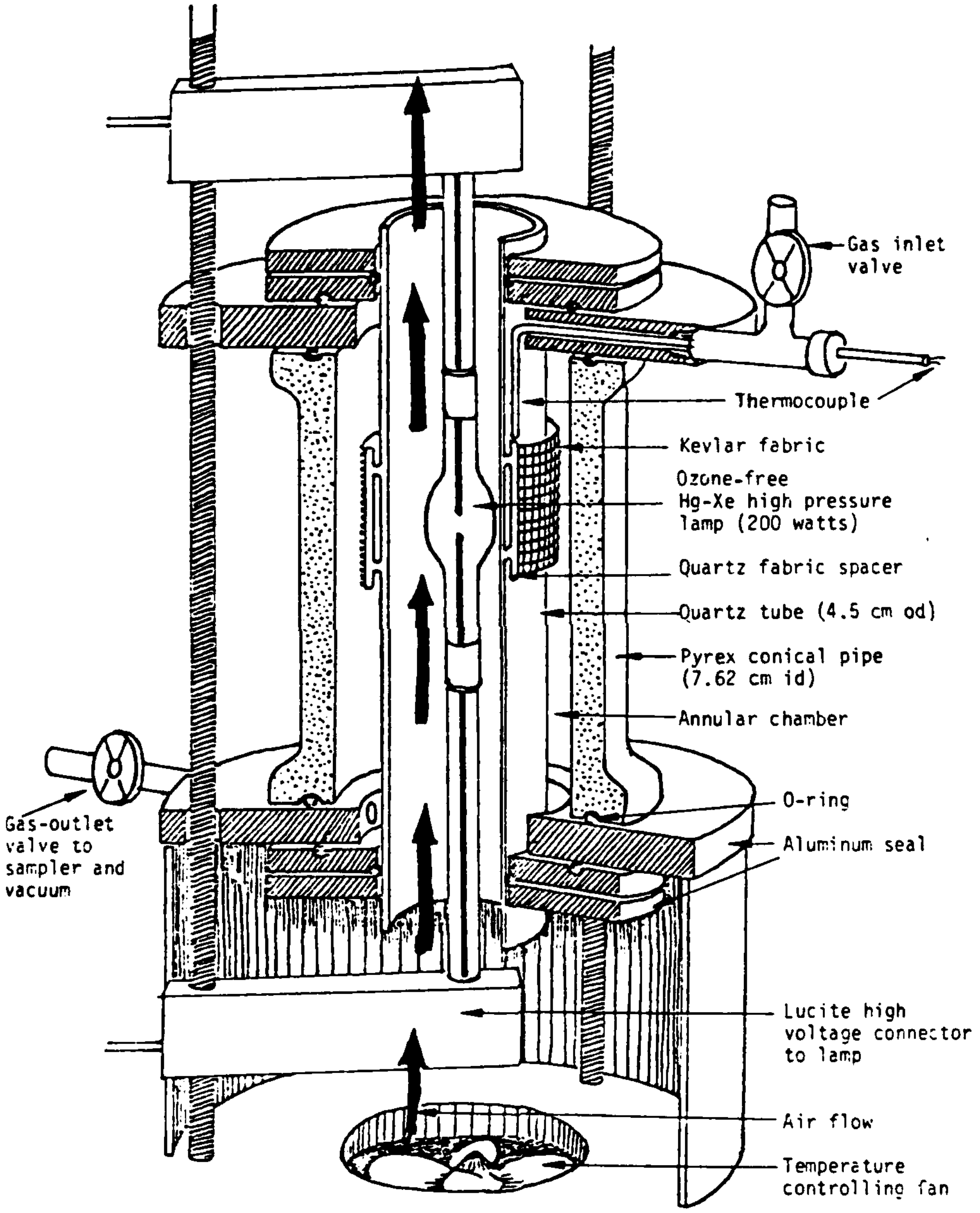


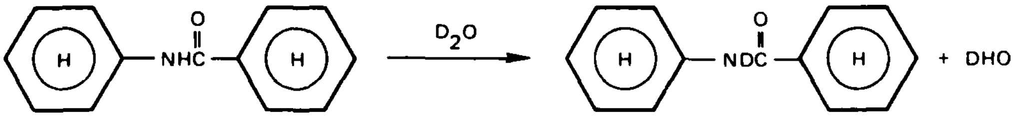
FIGURE 2. Schematic Longitudinal Section of Photolysis Chamber.

# THEORY OF OPERATION

## PHOTOOXIDATIVE STUDY BY $^1$HNMR

The dialkylamides were used as solvents to separate the photodegraded fabric surface molecules for analyses. The solutions were analyzed by $^1$HNMR in deuterated N,N-dimethylacetamide (DMA-$d_9$), deuterated N,N-dimethylformamide (DMF-$d_7$) or deuterated sulfuric acid ($D_2SO_4$).

Figure 3 shows the $^1$HNMR spectra of benzanilide solutions in $CDCl_3$ (a) and with $D_2O$ added (b). The H-chemical shift of the amide proton of III is at 7.8 ppm from TMS (tetramethylsilane) using an internal standard $CF_2ClCH_2Cl$ at 4.02 ppm from TMS. With the addition of a small amount of $D_2O$ to the solution, the NH-proton of benzanilide (III) becomes deuterated (Equation 1):



III IV (1)

Thus, the $^1$H-signal of III at 7.8 ppm disappears for IV.

Although the $^1$HNMR spectrum of the structural model (i.e., benzanilide) shows a proton resonance at 7.8 ppm, the $^1$HNMR spectra of the photodegraded Kevlar are broad at 7.8 ppm in deuterated dimethylacetamide, or deuterated dimethylformamide and deuterated sulfuric acid. The photodegraded Kevlar surface molecules apparently exhibit a gradient of molecular weights. The higher molecular weight fragments show rod-like character and cause solvent association and alignment in the magnetic field. These characteristics interfere with the $^1$HNMR resonance by broadening the sample signal. This problem can be reduced by further degrading the rod-like fragments in the solution, which then becomes resolvable by $^1$HNMR.

## AN ANALYTICAL STUDY OF PHOTODEGRADATED KEVLAR IN $^{18}O_2$ ATMOSPHERE

The oxidatively degraded products are concentrated on the fabric surface with an increase in the total terminal carboxylic acid end groups. This increase is caused by splitting of the amide linkages in the polymer chains on the surface layers. In the presence of oxygen-18-labeled atmosphere, each newly cleaved amide link generates one new carboxylic acid group containing one oxygen-18-labeled atom.

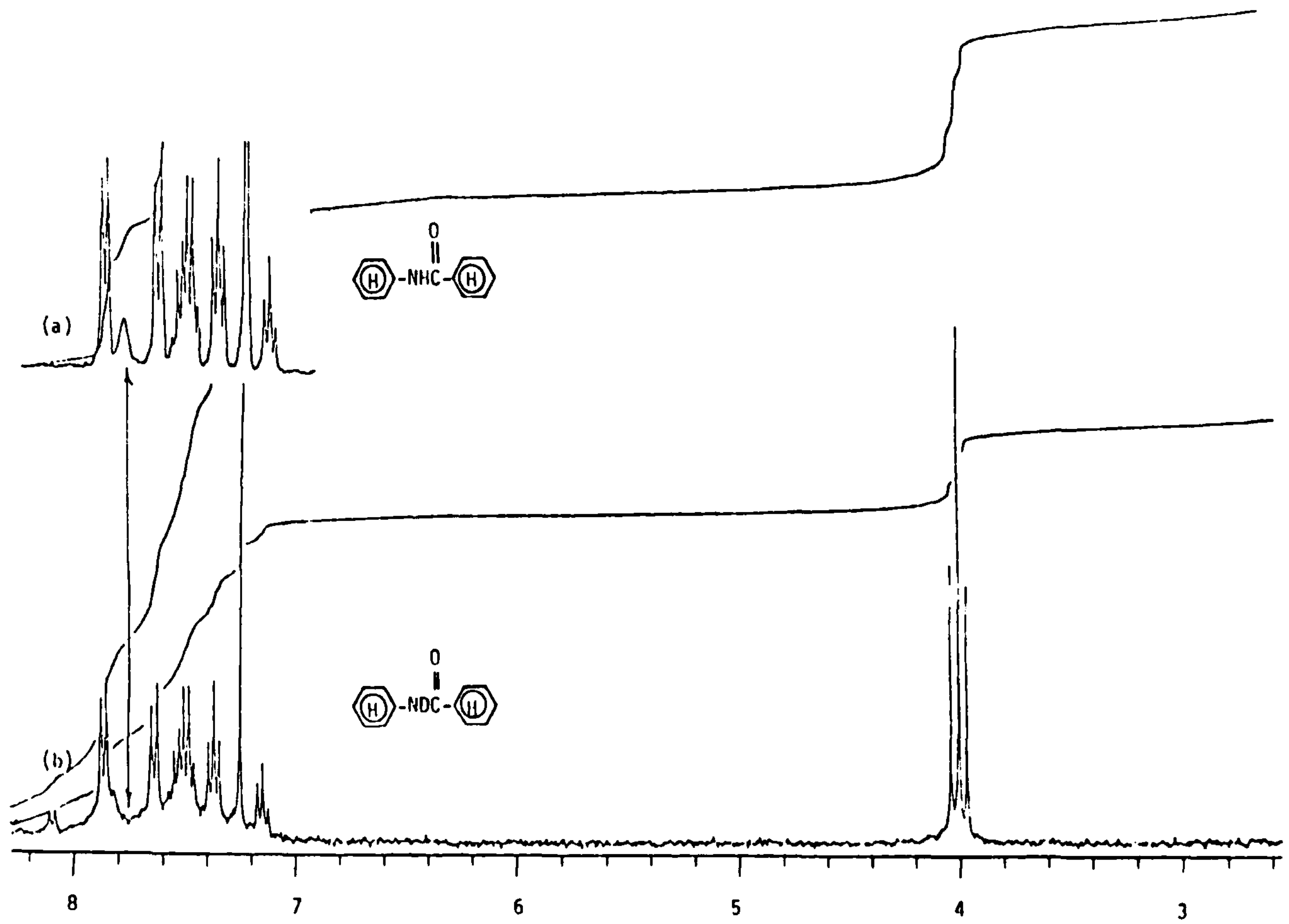
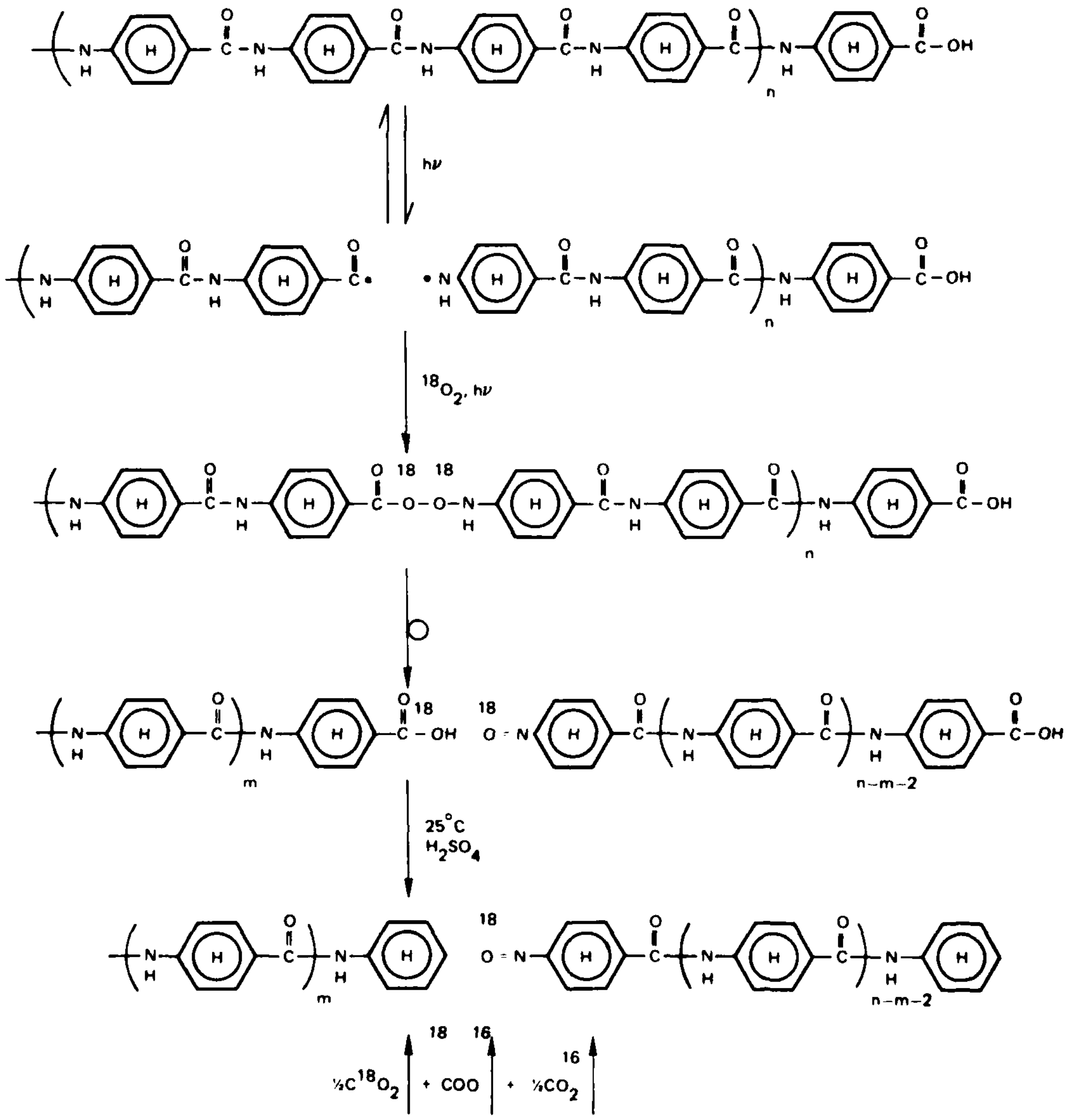


FIGURE 3. $^1$HNMR Spectra of Benzanilide in $CDCl_3$ (a) and With $D_2O$ Added (b).

The following reaction sequence (Equations 2 through 5) describes the photooxidative degradation mechanism of Kevlar in oxygen-18-labeled atmosphere:



(2)

(3)

(4)

(5)

The photodegradation process is initiated by the homolytic cleavages of the amide bond (Equation 2) (References 19 and 20), where $^{18}O_2$-insertion occurs before radical paired recombination (Equation 3). During the photooxidation, the type of oxygen-atom exchange, which was previously reported by Srinivasan and Noyes (Reference 21), occurring between $^{18}O_2$ and the carbonyl oxygen, may also occur here (Equation 3). This may be one possible path that explains the presence of $CO_2$ at mass 48 (Equation 5). The peroxide intermediate (Equation 3) rearranges to give an oxygen-18-labeled COOH and an oxygen-18-labeled nitroso end group. The latter is based on presumptive evidence caused by the labile nature of the nitroso compounds. The carboxylic acid groups are confirmed by infrared spectrophotometry. Decarboxylation occurs at 25°C (Equation 5). The total carbon dioxide content is measured by GC with a reference standard and the isotope ratio of $CO_2$ at mass 48, 46, and 44 by GC-mass spectroscopy. With these experimental data versus photolysis times and temperatures, the rate constant and activation energy can be calculated.

## EXPERIMENTAL

### REAGENTS

High purity air (ultra zero grade), oxygen (99.98%), and helium (99.99%) were purchased from Matheson; oxygen-18-labeled gas (99%) was purchased from ICON; a gaseous mixture of 100 ppm ethane in helium was purchased from Alltech; concentrated sulfuric acid (Ultrex) was purchased from J. T. Baker; 1,2-dichloro-1,1-difluoroethane was purchased from PCR; N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), and chloroform was purchased from Aldrich; and deuterated chloroform and fully deuterated DMF and DMAc was purchased from Stohler. The reagents were checked by infrared spectroscopy and used as-received unless otherwise specified.

### FABRIC CLEANING

The Kevlar-29 woven fabric was obtained through the courtesy of the Naval Weapons Center. The Kevlar-29 woven fabric is composed of 200-denier yellow yarn (Type 964) containing 134 zero twist filaments (each at a diameter slightly under 0.0013 cm) with a nominal yarn diameter of 0.2 mm assuming 70% packing factor (Reference 6). A special pair of serrated shears for cutting the fabric was purchased from Technology Associates. The fabric (2/5 cm × 18 cm) was placed in a Soxhlet thimble and extracted by 100 ml of chloroform for 24 hours to remove its surface lubricants (about 3% by weight). The fabric was then removed from the thimble and agitated in 20 ml of hot distilled DMAc for 15 minutes before it was placed back into the thimble and extracted for another 8 hours using fresh chloroform solvent. The solvent-cleaned fabric was dried in vacuo at room temperature.

### PHOTOLYSIS PROCEDURE

The solvent-cleaned Kevlar-29 fabric swatch (2.5 cm × 18 cm) was placed around the outside quartz tube inside the photolysis chamber, which was subsequently evacuated, before $^{18}O_2$ (99%) was introduced to 0.2 atm (the partial pressure of oxygen in the atmosphere). The photolysis chamber (Figure 2) was preheated to the specified photooxidation temperature before the Hg-Xe lamp was turned on. The temperature, which was held constant in the chamber by adjusting the airflow around the lamp, was monitored by a thermocouple placed next to the fabric sample inside the chamber. After the photooxidation had continued for the specified time period, the lamp was turned off and the photolysis chamber was evacuated and cooled to ambient temperature. Room air was let in and the photolysis chamber was opened to remove the oxidatively photodegraded fabric swatch. This procedure was repeated on different swatches at several temperatures versus photolysis times.

## SAMPLE PREPARATION FOR NMR ANALYSIS

After the solvent-cleaned fabric (about 3.5 cm × 18 cm or 400 mg) was photolyzed in air (i.e., $O_2$ at 0.2 atm), the degraded products on the fabric surface were dissolved in N,N-dimethylacetamide solvent (about 30 ml of distilled DMAc at 160°C). The DMAc solution was then dried in vacuo. The solid residue was dissolved in deuterated solvent (e.g., DMAc-$d_9$, N,N-dimethylformamide-$d_7$, or $D_2SO_4$) for $^1$HNMR analyses. The $^1$HNMR spectral data were obtained from a Nicolet spectrometer operating at 300 MHz and 35°C.

The $^{13}$CNMR analyses consisted of dissolving 0.1 g of surface-cleaned fabric in 10 ml of concentrated sulfuric acid in a 22 mm od and 203 mm length $^{13}$CNMR tube and measured from a Nicolet spectrometer operating at 75.5 MHz and 35°C. The extended degradation sample consisted of heating at 200°C for 3 hours to obtain a sulfuric acid solution of the sample.

## PREPARATION OF SOLUBLE SAMPLE FOR DECARBOXYLATION

The fabric surface was removed with a solvent. The photolyzed fabric swatch was placed in 20 ml of distilled DMSc at 110°C for 5 minutes. The DMAc solution was filtered to remove any insoluble fibrous material from the decarboxylation flask ( a round 30 ml two-neck Pyrex flask with a protruded bottom well) and dried in vacuo with the temperature kept below 50°C leaving a residual film on one side of the flask.

The purified sulfuric acid (i.e., preheated the commercial ultrapure grade $H_2SO_4$ at 200°C for 24 hours under vacuo to remove its decarboxylating contaminants and subsequently cooled to ambient temperature), 0.5 ml. was added to the bottom well of the decarboxylation flask and subsequently placed under vacuo. A known amount of a GC-standard (640 mm of 100 ppm $C_2H_6$ in He) was introduced into the flask for the total $CO_2$ determination. The acid was then allowed to dissolve the photodegraded residual film on the side of the flask by tilting. The acid solution was left standing for 20 minutes at room temperature.

## ANALYTICAL INSTRUMENTS FOR CARBON DIOXIDE ANALYSES

A gas chromatography (Carle Series 100) and GC-mass spectrometer (LKB9000) were used with identical GC-columns (2 mm id and 6 m length), which were purchased from Alltech and packed with 80% Porapak Q 80/100 and 20% Porapak N 80/100. The six-port mini-switching valve was purchased from Hach and used to trap the total carbon dioxide evolved and the $C_2H_6$ standard from the decarboxylation flask into its collection injection loop at liquid nitrogen temperature. This cold loop was warmed to ambient temperature and its trapped contents were vaporized. The collected vapor mixture in the loop was swept into the GC's helium stream (2 atm pressure) and into the column, and then into the thermister detector when the valve was turned to injection mode. The sample was analyzed for the total $CO_2$ content and the $C_2H_6$ standard. After the $CO_2$ had passed through the GC's detector, the vapor mixture was then collected in a portable gas cell, which consisted of a six-port mini-switching valve and a collection/injection loop, again chilled to liquid nitrogen temperature.

The collected sample at − 196 °C was isolated from the flow of the GC's helium gas stream and then the loop was warmed to ambient temperature for GC-mass spectroscopic analyses. The gas cell, which contained the isotopic $CO_2$ and the $C_2H_6$ standard in helium at 1 atm, was placed in the injection helium flow of the GC-mass spectrometer for 10 minutes before the mini-switching valve was turned to inject the vapor contents into the instrument. After 3 minutes, the $CO_2$ peak eluted. The superimposed peaks were sampled ten times during their elution and the relative isotopic quantities of $^{45}CO_2$, $^{46}CO_2$, $^{47}CO_2$ and $^{48}CO_2$ were determined.

## RESULTS AND DISCUSSION

### NMR STUDIES

The $^1$HNMR spectrum of the structural model (i.e., benzanilide in $CDCl_3$ in the absence of $D_2O$) shows a sharp proton resonance at 7.8 ppm from TMS indicating the NH-group; whereas in the presence of $D_2O$ the 7.8 ppm peak disappears due to the deuterium exchange of the amide proton (in the section entitled "Photooxidative Study by HNMR" and Figure 3). Although the $^1$HNMR at 7.8 ppm of the oxidatively photodegraded Kevlar sample in the deuterated solvent was broadened when compared to the model compound, an approximation was still feasible.

The data are described below. Figure 4 shows the weight loss data of Kevlar, which were deduced from the relative areas of $^1$HNMR at 7.8 ppm versus photolysis times. The initial rate was determined as $1.6 \times 10^{-5}$ g/solar-hour/g-Kevlar and after 625 solar hours as $3.8 \times 10^{-7}$ g/solar-hour/g-Kevlar. In this experiment, the photolysis chamber temperature was calculated from P-V-T measurements, assuming ideal gas behavior. The other data and estimations are as follows:

Volume of NMR sample = 0.5 ml = 0.5/1000 liter

Amount of standard $CF_2ClCH_2Cl$ added = 0.0208 mole/liter
(An equivalent of hydrogen-content in standard as 2 = 0.0416 mole/liter)

The relative area of the $^1$HNMR resonance of the standard at 4.02 ppm = 4.8

Mole weight of the moiety $+C_7H_5NO+$ = 119 g/mole

The relative area of the $^1$HNMR resonance for photodegraded Kevlar at 7.8 ppm

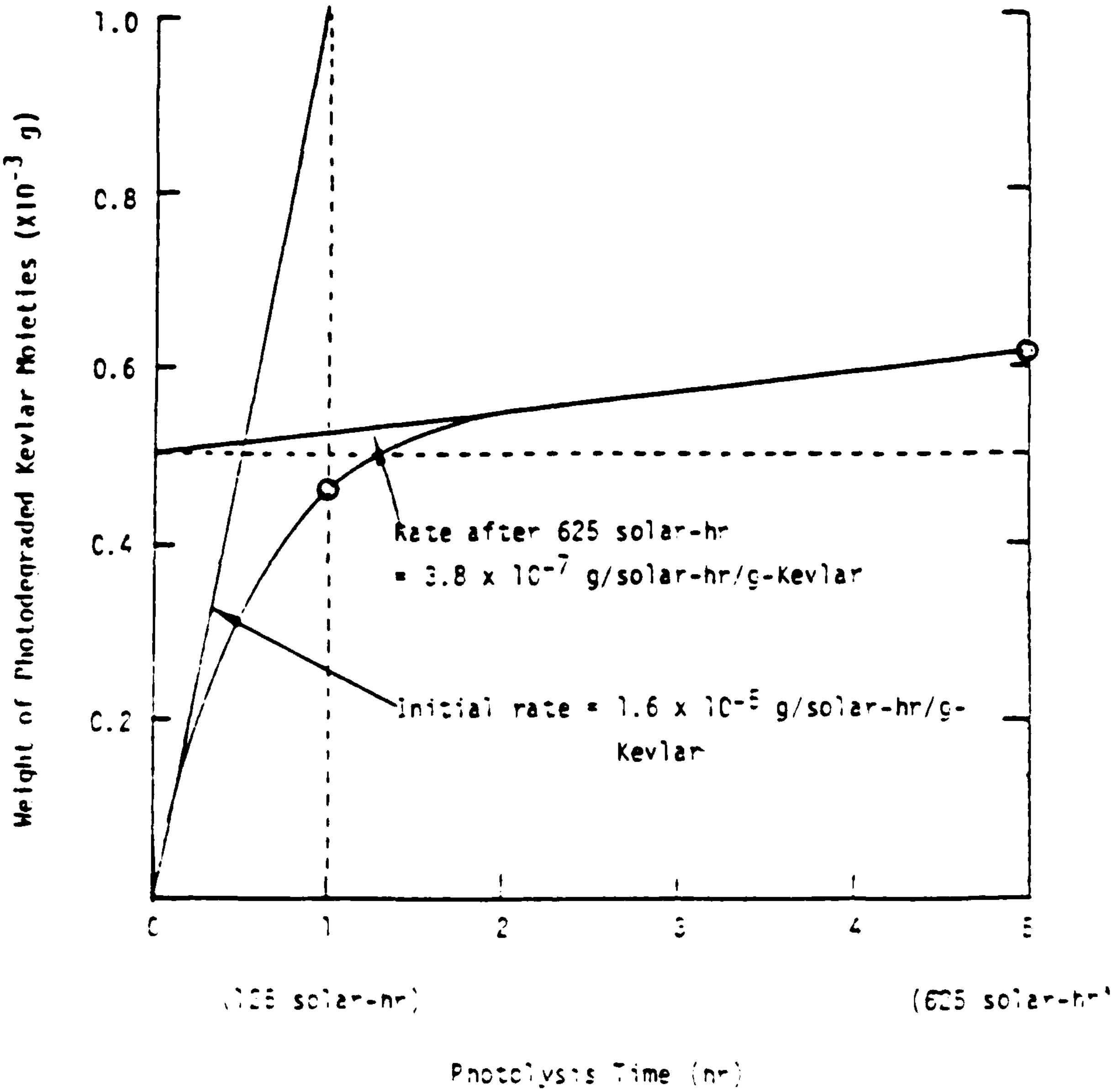


FIGURE 4. Weight of the Photodegraded Kevlar Moieties Versus Photolysis Time at 52.0 ± 1.5°C.

After 1 hour (i.e., 125 solar hours at air mass 2) = 0.9

After 5 hours (i.e., 625 solar hours at air mass 2) = 1.2

The calculated weight loss of Kevlar after 125 solar hours

$$= \frac{0.9}{4.8} \times 0.0416 \text{ mole/l} \times 119 \text{ g/mole} \times \frac{0.5}{1000} \text{ l}$$

$$= 4.70 \times 10^{-4} \text{ g (equivalent to four monolayers of Kevlar fabric)}$$

The calculated weight loss of Kevlar after 625 solar hours

$$= \frac{1.2}{4.8} \times 0.0416 \times 119 \times \frac{0.5}{1000}$$

$$= 6.19 \times 10^{-4} \text{ g (equivalent to six monolayers of Kevlar fabric)}$$

From Figure 4, the initial rate (i.e., 125 solar hours at air mass 2)

$$\text{of 0.5 g Kevlar-29 fabric sample} = \frac{1.0 \times 10^{-3} \text{ g}}{125 \text{ solar hours}}$$

$$= 8 \times 10^{-6} \text{ g/solar-hour}$$

$$\text{of 1.0 g Kevlar-29 fabric sample} = 1.6 \times 10^{-5} \text{ g/solar-hour}$$

From Figure 4, the rate after 5 hours (i.e., 625 solar hours at air mass 2)

$$\text{of 0.5 g Kevlar-29 fabric sample} = \frac{(0.619 - 0.5 \times 10^{-3} \text{ g})}{625 \text{ solar hours}}$$

$$= 1.9 \times 10^{-7} \text{ g/solar-hour}$$

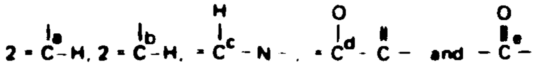
$$\text{of 1.0 g Kevlar-29 fabric sample} = 3.8 \times 10^{-7} \text{ g/solar-hour}$$

In conclusion, the photodegradation rate

$$\text{after 625 solar hours} = \frac{3.8 \times 10^{-7} \times 100}{1.6 \times 10^{-5}} = 2\% \text{ the initial rate (or 1/50th the initial rate)}$$

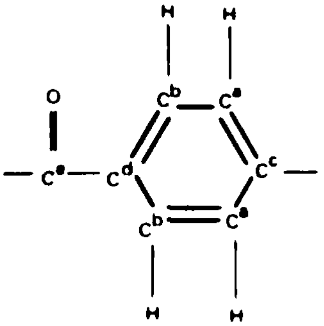
The activation energy was estimated at 2.3 kcal/mole from weight loss of Kevlar fabric versus photolysis time of 5 hours (625 solar hours) at 52°C and 130°C runs.

The extended degradation sample consisted of adding 10 ml of concentrated sulfuric acid to 0.1 g of the Kevlar fabric and then heating the mixture to 200°C for 3 hours to obtain the sulfuric acid solution. The five carbon resonances were observed at 126, 130.5, 133, 134.5 and 193 ppm from TMS and assigned to



$$2 = \overset{|_a}{C}-H,\ 2 = \overset{|_b}{C}-H,\ = \overset{\overset{H}{|}}{C^c}-N-,\ = \overset{\overset{O}{|}}{C^d}-\overset{\|}{C}-\ \text{and}\ -\overset{\overset{O}{\|}}{C^e}-$$

at the area ratio of 2:2:1:1:1, respectively, for the seven carbon atom structure:



The $^{13}$CNMR spectrum differentiates the carbon atoms and is an improvement over the broad absorption of $^1$HNMR at 7.8 ppm. Its disadvantage is the large sample size requirement.

## OXIDATION IN $^{18}O_2$ ATMOSPHERE

The oxidation under daylight exposures is a continuous ongoing process that influences the Kevlar sample. The use of $^{18}O_2$ atmosphere allows the differentiation between the accelerated experimental photooxidation conditions and its usual room exposure effects. This paper determines the rates of photooxidations of Kevlar-29 fabric based on the oxygen-18-labeled carbon dioxide (i.e., $^{46}CO_2$ and $^{48}CO_2$ isotopes) decarboxylated from the Kevlar sample. In other words, the oxygen-18-labeled atoms, which are inserted in the Kevlar macromolecules, are being analyzed to determine the photodegradation processes.

The photodegraded Kevlar macromolecules in an $^{18}O_2$ atmosphere were removed by a solvent, then dried in vacuo to a solid film, and decarboxylated in concentrated sulfuric acid at 25 °C and 196°C. The data on the total $CO_2$ evolved and the isotopic $CO_2$ ratios provide the information on the extent of the degradation, the distribution of the oxygen-18-labeled Kevlar moieties, and the types of the photooxidative degradation.

At 25°C, the Kevlar macromolecule retains its polymeric structure in concentrated sulfuric acid solvent. The rapid decarboxylation observed at 25°C in Table 2 appears to originate from the oxidized terminal groups of the macromolecules (References 8 and 22). In contrast, the acid decarboxylation at 196°C appears to break down the Kevlar macromolecules completely. A thermal degradation pattern has been recognized for the decarboxylation of Kevlar in sulfuric acid at 196°C, whether the fabric was exposed to photolysis in the chamber or not. This thermal decomposition pattern is used as a decarboxylation model, which constitutes the same two types of decarboxylation reactions at 196°C (e.g., R1 and R2 in Table 2): one yields 1

TABLE 2. Decarboxylation Data of Photodegraded Kevlar (Exposed for 7 Minutes at 100°C in 0.2 atm $^{18}O_2$ in the Photolysis Chamber).

| $CO_2$ Isotope | Decarboxylation[a] at | | | |
|---|---|---|---|---|
| | 25°C | | 196°C | |
| | Moles of total $CO_2$ evolved | Rate of $CO_2$ evolution, $t_{1/2}$, min | Moles of total $CO_2$ evolved[b] | Rate of $CO_2$ evolution, $t_{1/2}$ |
| $^{44}CO_2$ | $1.6 \times 10^{-4}$ | 1 to 10 | $6.98 \times 10^{-3}$<br>$3.49 \times 10^{-3}$ | Two types of reactions[c]:<br>(R1) 660 hr<br>(R2) 4 to 12 hr |
| $^{46}CO_2$ | $1.9 \times 10^{-9}$ | 1 to 10 | $4.0 \times 10^{-7}$ | 42 hr[d] |
| $^{48}CO_2$ | $7.0 \times 10^{-11}$ | 1 to 10 | $4.3 \times 10^{-9}$ | 8 min |

[a] The total carbon available for decarboxylation from 0.415 g Kevlar fabric sample [expressed as $+C_7H_5NO+$ moieties in moles; i.e., $3.49 \times 10^{-3}$ moles] = $3 \times 3.49 \times 10^{-3} = 1.05 \times 10^{-4}$ moles, where 3 designates three carbon atoms from a $+C_7H_5NO+$ moiety of 7 carbons eliminating as $CO_2$.

[b] Includes extrapolated data.

[c] There are consistently two types of decarboxylation reactions that occur at 196°C (R1 and R2) of a given Kevlar sample [expressed as $+C_7H_5NO+$ moieties in moles], whether it was exposed or not exposed to photolysis: one yields one mole of $CO_2$ per $+C_7H_5NO+$ moiety and the other gives two moles of $CO_2$ per $+C_7H_5NO+$ moiety (e.g., Figure 5).

[d] Two rates (a fast and a slow) may be involved.

mole of $CO_2$ per $+C_7H_5NO+$ moiety and the other gives 2 moles of $CO_2$ per $+C_7H_5NO+$ moiety. The half life of the former is 4 to 12 hours and appears to originate from the amide linkages' carbonyl groups. The latter's half life is 660 hours and is from two of the six carbons of its aromatic rings.

Figure 5 shows the types of decarboxylation (R1 and R2) as the pseudo first order reactions. Since the bimolecular second order process (decarboxylation of Kevlar in concentrated $H_2SO_4$) contains one of the reactants (concentrated $H_2SO_4$) in great excess to the other reactant (the solvated surface layer). Figure 5 also illustrates the changes in concentrations with times of R1 and R2. The R2 intercept is $32 \times 10^{-6}$ moles, i.e., the initial concentration at R2 at about $11 \times 10^{-6}$ and the initial concentration of R1 at about $21 \times 10^{-6}$ moles. The ratio of R1 and R2 reactions is about 2:1, which conforms with all the decarboxylation reactions (e.g., Table 2) at 196°C, whether the Kevlar sample was or was not exposed to photolysis chamber conditions. Consistently, three moles of $CO_2$ evolved per $+C_7H_5NO+$ moiety of seven carbons eliminating as one mole $CO_2$ at $t_{1/2}$ of 4 to 12 hours (R2) and two moles $CO_2$ at $t_{1/2}$ of 660 hours (R1).

Table 2 also shows that the main component of the total $CO_2$ evolved, which is determined by GC, is the regular $^{44}CO_2$, and the total of the other $CO_2$ isotopes (e.g., $^{46}CO_2$ and $^{48}CO_2$) is about $10^{-4}$ of $CO_2$. The low concentrations of the isotopic $^{46}CO_2$ and $^{48}CO_2$ are

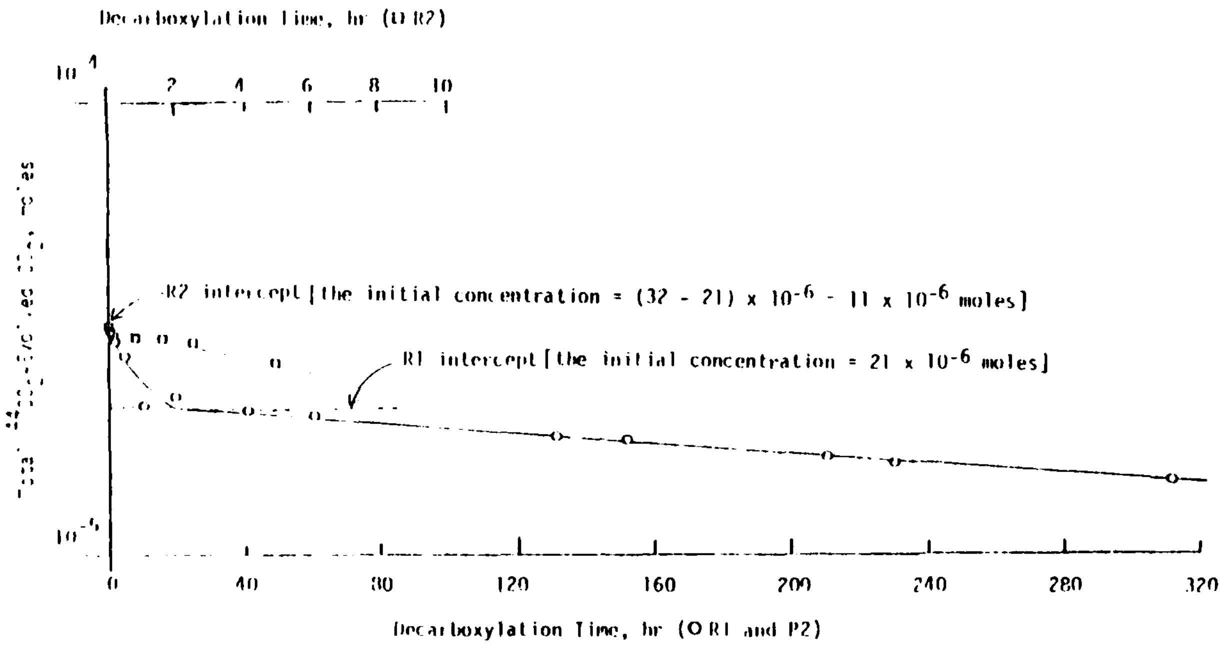
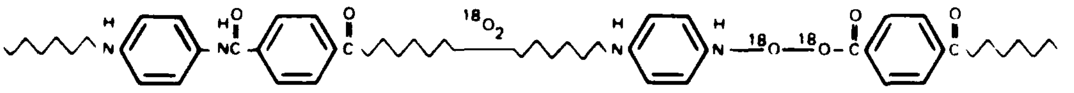


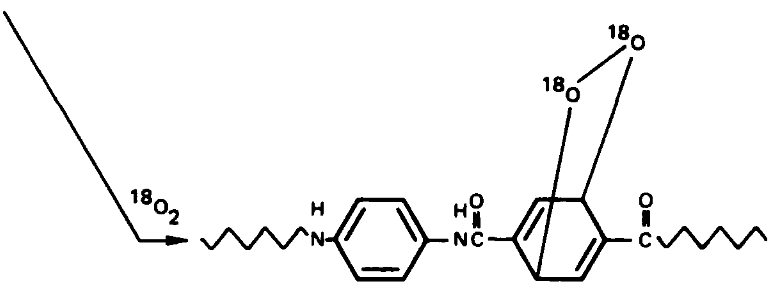
FIGURE 5. A Representative Plot of $^{44}CO_2$ Concentration Versus Decarboxylation Time for the Two Types of Pseudo First Order Decarboxylation Reactions at 196°C. The ratio R2 intercept over R1 intercept is 1:2.

still, however, an easily measurable quantity by GC-mass spectrometer. The $^{45}CO_2$ is used as the standard, because the measurement of $^{45}CO_2$ relates directly to the quantity of the abundant $^{44}$ $CO_2$. Its low concentration levels help to improve the measuring accuracy of the other $CO_2$ isotopes, which are also in low concentration. The moles of the total $CO_2$ from the GC determination is used for the calculation of the moles of $^{45}CO_2$ as follows:

$$\text{Moles of the total } CO_2 \times 0.01108 = \text{moles of } ^{45}CO_2$$

where 0.01108 is the fraction of $^{13}C$ in carbon at mass 12. The presence of $^{46}CO_2$ and $^{48}CO_2$ are measured from their respective peak areas compared to that of $^{45}CO_2$. The moles of $^{46}CO_2$ and $^{48}CO_2$ are then corrected by subtracting the $^{46}CO_2$ and $^{48}CO_2$ occurring naturally in the $CO_2$ sample. Some of the possible photooxidized sites of the Kevlar macromolecules before decarboxylation are illustrated below (Equations 6 and 7).

 (6)



(7)

These $^{18}O_2$-inserted macromolecules can be differentiated from the ongoing $^{16}O_2$-oxidized macromolecules by GC-mass spectrometer.

When a sample of the same Kevlar-29 fabric was identically treated in $^{18}O_2$ atmosphere except in the absence of photolysis (in the dark) for 24 hours, the results of $CO_2$ evolved at 25° and 196°C from the GAC-analysis were the same as the samples under photolysis (i.e., Table 2). However, the gross difference was in the analyses of the GC-mass spectroscopic data, where no oxygen-18-labeled $CO_2$ isotopes evolved (i.e., there was no $^{46}CO_2$ or $^{48}CO_2$ above the natural background levels).

Figures 6 and 7 illustrate the pseudo first order decarboxylation reactions of $^{46}CO_2$ (the slow reaction with $t_{1/2}$ = 42 hours) and $^{48}CO_2$ (the fast reaction with $t_{1/2}$ = 8 minutes). The photodegraded sample was exposed for 7 minutes at 100°C in 0.2 atm $^{18}O_2$. The concentration of $^{18}O$-Kevlar is expressed as $-(C_7H_5NO)-$ in moles and is equal to the total $^{46}CO_2$ minus evolved $^{46}CO_2$ in moles for Figure 6 and $^{48}CO_2$ minus evolved $^{48}CO_2$ in moles for Figure 7.

Figure 8 shows the radial $^{18}O$-distribution from the fiber surface toward the fiber center (0.00065 cm). The area under the curves are the total mole ratios $^{46}CO_2/-(C_7H_5NO)-$ at $1.15 \times 10^{-4}$ for curve (a) and $^{48}CO_2/-(C_7H_5NO)-$ at $1.23 \times 10^{-5}$ for curve (b). Most of the $^{48}CO_2$ (95%) was evolved during the first 30 minutes. Successive surface layers, which were then dissolved separately in distilled DMAc solvent and decarboxylated in concentrated sulfuric acid, were analyzed for $^{46}CO_2$ and $^{48}CO_2$. Although the most severely photodegraded part of the fiber occurred at the light exposed surface, it appeared that the $^{18}O$-distributions were present throughout the fiber. Table 3 summarizes the decarboxylation data of Kevlar and its radial distribution of oxygen as a constituent in $^{44}CO_2$, $^{46}CO_2$, and $^{48}CO_2$. The data were obtained from 0.415 g Kevlar-29 fabric, which was expressed as $-(C_7H_5NO)-$ in moles ($3.49 \times 10^{-3}$ moles) and was exposed for 7 minutes at 100°C in 0.2 atm $^{18}O_2$ in the photolysis chamber. The isotopic $^{46}CO_2$ decarboxylation reactions at 196°C and 25°C diminished toward the fiber center. The concentration of $^{46}CO_2$ per $-(C_7H_5NO)-$ moiety was highest near the outer fiber surface. The isotopic $^{48}CO_2$ was found only in the outermost surface for the rapid decarboxylation reaction at 25°C, but at 196°C the concentration of $^{48}CO_2$ per $-(C_7H_5NO)-$ moiety was also present throughout the fiber. By using the radial $^{18}O$-distribution data in Table 3, the other photodegraded sample at different photolysis times and temperatures can be estimated from the surface analyses alone by assuming similar $^{18}O$-distributions. Further work and verification in this area are recommended.

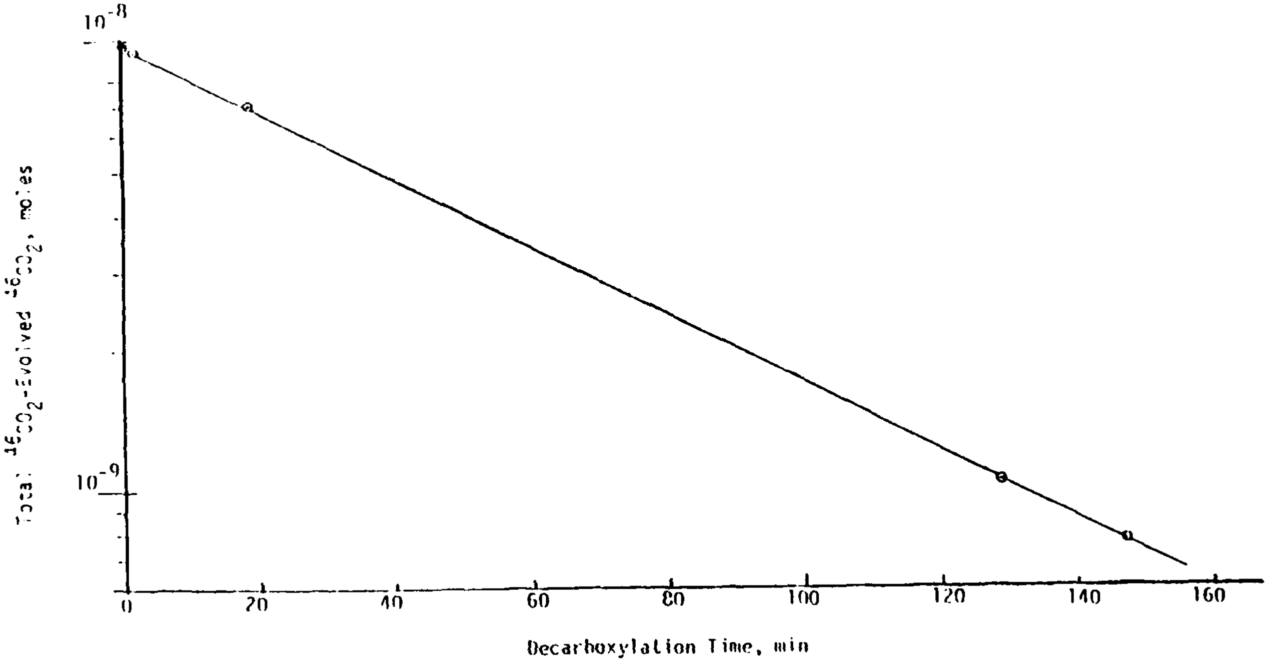


FIGURE 6. An Example of $^{46}CO_2$ Concentration Versus Decarboxylation Time for Pseudo First Order Reaction at 196°C.

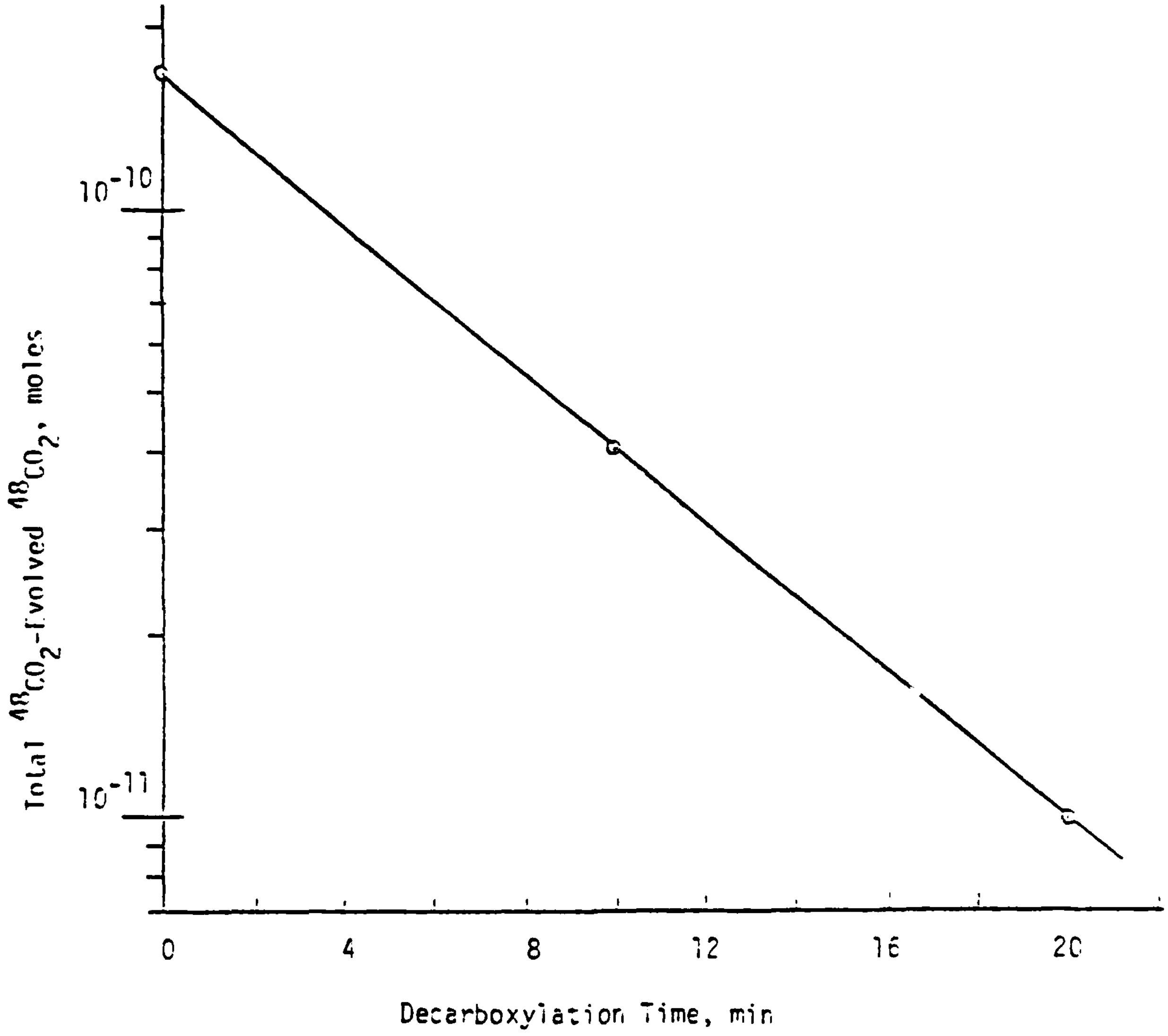


FIGURE 7. An Example Plot of $^{48}CO_2$ Concentration Versus Decarboxylation Time for Pseudo First Order Reaction at 196°C.

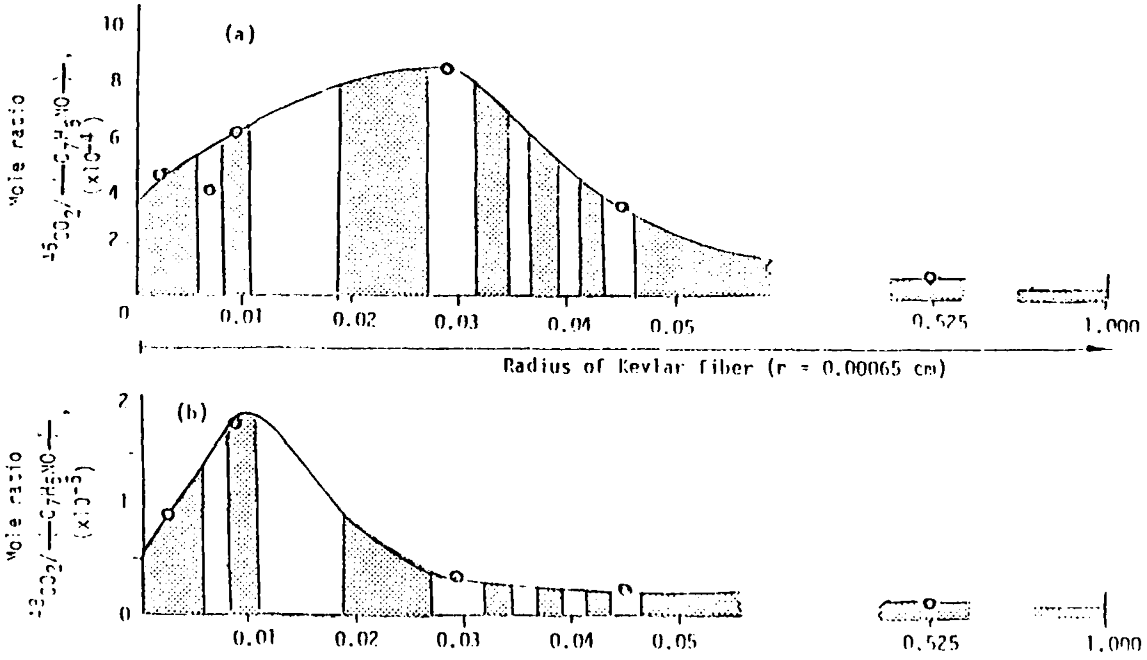


FIGURE 8. The Average Radial $^{18}O$-Distribution, Which Contributed to $^{46}CO_2$ (a) and $^{48}CO_2$ (b) Measurements for the Two Major Oxidative Processes.

TABLE 3. Summary Data on Decarboxylation of Kevlar and its Radial Distribution of Oxygen (as a Constituent in $^{44}CO_2$, $^{46}CO_2$ and $^{48}CO_2$).

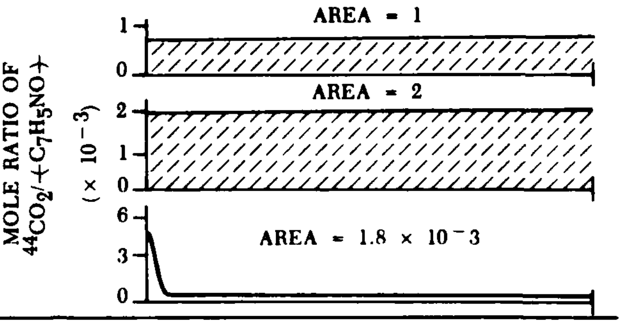
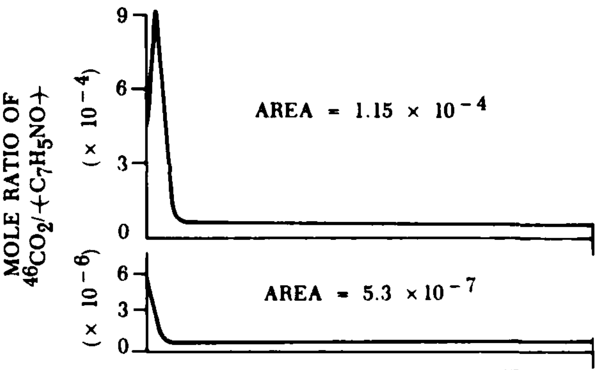
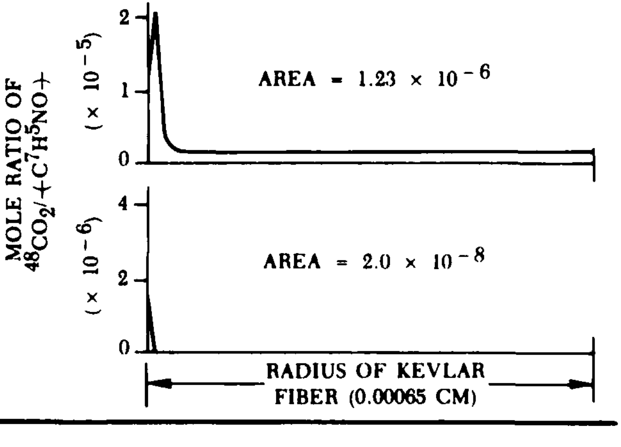
| $CO_2$ species | Decarboxylation temp, °C | Half life, $t_{1/2}$ | Radial distribution in Kevlar fiber, area under the curve = $CO_2$ species/mole $+C_7H_5NO+$ |
|---|---|---|---|
| $^{44}CO_2$ ..... | 196 | (R2) 4 to 12 hr |  |
|  | 25 | 1 to 10 min |  |
|  | 196 | (R1) 660 hr |  |
| $^{46}CO_2$ ..... | 196 | 42 hr |  |
|  | 25 | 1 to 10 min |  |
| $^{48}CO_2$ ..... | 196 | 8 min |  |
|  | 25 | 1 to 10 min |  |

Table 4 lists the photooxidation rates, which were deduced from four pseudo first order decarboxylations of $^{46}CO_2$ at 196°C and 25°C and $^{48}CO_2$ at 196°Cand 25°C. The initial concentrations of $-(C_7H_5NO-)_n$ to produce 1/2 mole $^{18}O_2$ (i.e., to produce $^{46}CO_2$ product) is 6.1 mole/l and to produce 1 mole $^{18}O_2$ (i.e., to produce $^{48}CO_2$ product) is 12.2 mole/l using the density of Kevlar at 1.45 g/cc. The $^{18}O_2$ is assumed as an ideal gas at 100°C and 0.2 atm. The 0.415 g Kevlar-29 fabric expressed as $-(C_7H_5NO)-$ moieties in moles is $3.49 \times 10^{-3}$ moles.

Figure 9 shows the plots of the two major photooxidation processes versus photolysis time and temperature. Table 5 summarizes the two major photooxidative degradation rate constants and activation energies.

## CONCLUSIONS

The $^1$HNMR study of the photodegraded Kevlar solutions has problems even in the high dilutions. Only broad resonance signals are observed, thus this is not a useful method to pursue further.

The preferred method is to carry out the photodegradation in an $^{18}O_2$ atmosphere. The new and novel method to study the photochemical degradation of Kevlar-29 fabric in air divides into four steps:

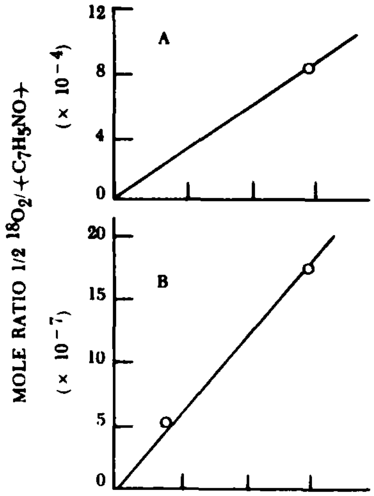
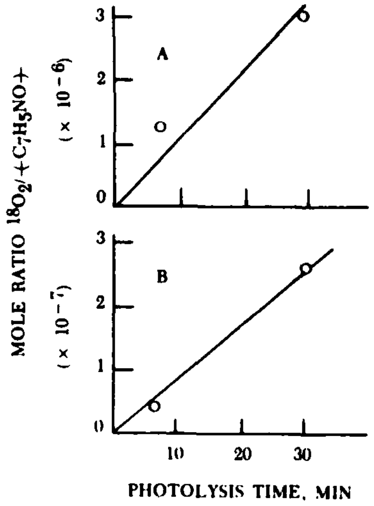
1. Fabric cleaning
2. Photolysis at specified temperature and time in 0.2 atm $^{18}O_2$
3. Preparation of the degraded (DMAc-solute) sample surface for decarboxylation at 25°C and 196°C in the concentrated sulfuric acid
4. The total carbon dioxide analysis by gas chromatography and isotope carbon dioxide ($^{46}CO_2$ and $^{48}CO_2$) ratios by GC-mass spectroscopy

The first significant accomplishment of this project was the new and novel analytical approach, which demonstrated the rate constant and activation energy determinations of Kevlar's photooxidative processes. The 0.2 atm of oxygen-18-labeled environment in a solar chamber simulates the air exposure under sunlight conditions. The technique also allows the radial $^{18}O$-distribution measurement from the fiber surface toward the fiber center. The data from the accelerated experimental conditions in the solar chamber in an $^{18}O_2$-atmosphere are differentiated from the similar ambient daylight exposure effects.

The second significant accomplishment was the recognition of a thermal decomposition pattern of Kevlar in concentrated sulfuric acid at 196°C to give the same two types of decarboxylations: one yields one mole of $CO_2$ per $-(C_7H_5NO)-$ moiety and the other gives two moles of $CO_2$ per $-(C_7H_5NO)-$ moiety. The half life of the former is 4 to 12 hours and appears to originate from the amide linkages' carbonyl groups. The latter's half life is 660 hours and is from two of the six carbons of its aromatic rings.

The third significant accomplishment was the analytical methodology applied to deduce the four photooxidative processes. The data on the total $CO_2$ evolved from the samples were measured by gas chromatography and the isotopic $CO_2$ ($^{46}CO_2$ and $^{48}CO_2$) data by GC-mass

TABLE 4. Photooxidation Rates at 100°C of Pseudo First Order Decarboxylations.

| Plots of 1/2 $^{18}O_2$ and $^{18}O_2$ concentrations vs. photolysis times[a] | Photolysis rates[b], mole $s^{-1}$ | Solar rates[c], mole $s^{-1}$ | Rate constants of 2nd order photooxidation of Kevlar[d] in 0.2 atm $^{18}O_2$ at 100°C, l $mole^{-1}$ $s^{-1}$ |
|---|---|---|---|
|  | $1.65 \times 10^{-9}$<br>$3.28 \times 10^{-12}$ | $1.32 \times 10^{-11}$<br>$2.62 \times 10^{-14}$ | $4.18 \times 10^{-8}$ |
|  | $5.82 \times 10^{-12}$<br>$5.04 \times 10^{-13}$ | $4.67 \times 10^{-14}$<br>$4.03 \times 10^{15}$ | $2.01 \times 10^{-10}$ |

[a] 'A' designates decarboxylation temperature at 196°C and 'B' at 25°C.

[b] Photolysis rates are expressed as moles of +$C_7H_5NO$+/photolysis times (sec).

[c] Solar rates are photolysis rates/125.

[d] The initial concentrations of +$C_7H_5NO$+$_n$ to produce 1/2 $^{18}O_2$ (i.e., to produce $^{46}O_2$ product) is 6.1 mole $l^{-1}$ and to produce $^{18}O_2$ (i.e., to produce $^{48}CO_2$ product) is 12.2 mole $l^{-1}$ using the density of Kevlar at 1.45 g/$cm^3$. The $^{18}O_2$ is assumed as an ideal gas at 100°C and 0.2 atm. the 0.415 g Kevlar-29 fabric expressed as +$C_7H_5NO$+ moieties in moles is $3.49 \times 10^{-3}$ moles.

See the Appendix for calculation.

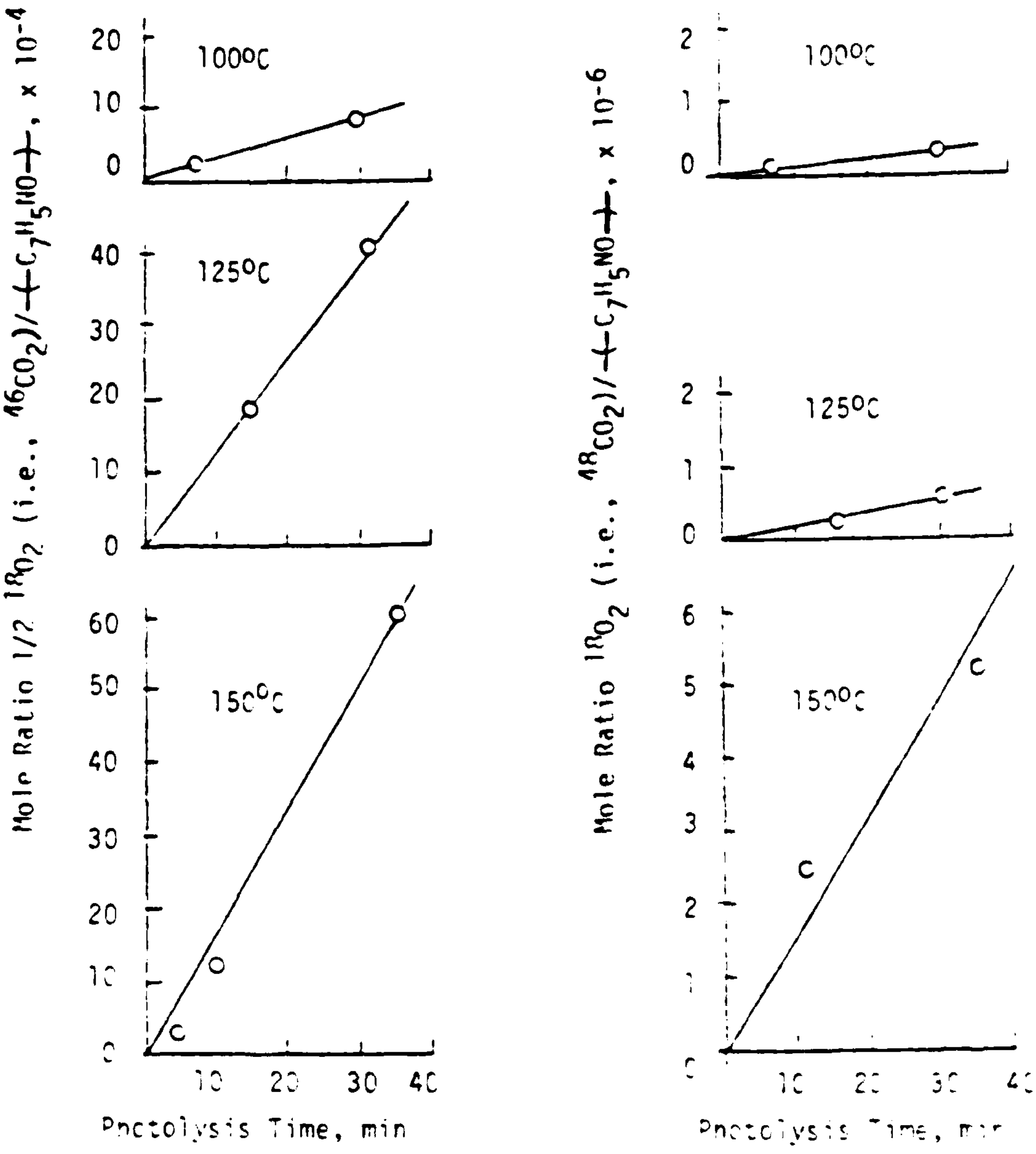


FIGURE 9. Plots of Oxygen-18 Concentration Versus Photolysis Time of Pseudo First Order Decarboxylations at 198°C for 20 Minutes From the Top Surface Layer

TABLE 5. Summary Data on the Two Major Photooxidative Degradation Rate Constants and Activation Energies[a]

| Temperatures | | | Photolysis rates,[b] mole sec$^{-1}$ | Solar rates,[c] mole sec$^{-1}$ | Rate constants,[d] l mole$^{-1}$ sec$^{-1}$ | Activation energies,[e] kcal mole$^{-1}$ |
|---|---|---|---|---|---|---|
| °C | °K | 1000/°K | | | | |
| I. From plots of 1/2 $^{18}O_2$ (i.e., $^{46}CO_2$) concentrations versus photolysis times (Figure 5 LEFT) | | | | | | |
| 25 | 298 | 3.356 | | | $1.10 \times 10^{-8}$ | |
| 100 | 373 | 2.681 | $1.65 \times 10^{-9}$ | $1.32 \times 10^{-11}$ | $4.18 \times 10^{-8}$ | |
| 125 | 398 | 2.513 | $7.76 \times 10^{-9}$ | $6.21 \times 10^{-11}$ | $1.96 \times 10^{-7}$ | |
| 150 | 423 | 2.364 | $9.69 \times 10^{-9}$ | $7.75 \times 10^{-11}$ | $2.36 \times 10^{-7}$ | 10.8 |
| II. From plots of $^{18}O_2$ (i.e., $^{48}CO_2$) concentrations versus photolysis times (Figure 5 RIGHT) | | | | | | |
| 25 | 298 | 3.356 | | | $1.03 \times 10^{-12}$ | |
| 100 | 373 | 2.681 | $5.82 \times 10^{-12}$ | $4.66 \times 10^{-14}$ | $2.0 \times 10^{-10}$ | |
| 125 | 398 | 2.513 | $9.69 \times 10^{-12}$ | $7.75 \times 10^{-14}$ | $2.37 \times 10^{-10}$ | |
| 150 | 423 | 2.364 | $9.69 \times 10^{-11}$ | $7.75 \times 10^{-13}$ | $2.43 \times 10^{-9}$ | 15.7 |

[a] Data are deduced from pseudo first order decarboxylations at 196°C for 20 min from the top surface layer of the photolyzed Kevlar.

[b,c,d] Same as footnotes b, c, d of Table 4.

[e] Activation energies are calculated from photolyses runs at 100° and 150° using calculated rate constants (column 4) at the two temperatures by $\Delta E = (RT_1T_2/T_2 - T_1) \ln (k_2/k_1)$.

spectroscopy. The rate constants of the two major photooxidative degradation processes at 25°C were deduced from 1/2 $^{18}O_2$ per $+C_7H_5NO+$ (i.e., to produce $^{46}CO_2$ product, $t_{1/2}$ = 42 hours at 196°C and the other from $^{18}O_2$ per $+C_7H_5NO+$ (i.e., to produce $^{48}CO_2$ product, $t_{1/2}$ = 8 minutes) at 196°C. The rate constants of the former process was estimated as $1.10 \times 10^{-8}$ l mole$^{-1}$ second$^{-1}$ and the latter as $1.03 \times 10^{-12}$ l mole$^{-1}$ second$^{-1}$. The activation energies of these two processes were deduced as 10.8 kcal/mole for the former and 15.7 kcal/mole for the latter.

## RECOMMENDATION

Further research by the solution sample approach of the $^1$HNMR method for the photodegraded Kevlar study is not recommended. Carrying out the photodegradation in an $^{18}O_2$ atmosphere is the preferred analytical approach. This novel approach was conceived during the course of this project study and this new technique was developed to a stage where the oxidative degradation process of Kevlar-29 fabric in air under the sun were characterized. Because limited time and effort was available toward the end of this project, the rate constants and activation energy numbers should be confirmed with more data. In the area of radial $^{18}O$-distribution in the Kevlar fiber, an assumption was made that this distribution is similar at the different photolysis temperatures and times. This assumption should be supported with experimental data.

Future work is recommended to apply this technique of photochemical degradation in simulated air under the sun to other fabric and polymer film studies. The investigation on photodegradation of Kevlar-29 fabric in a vacuum is warranted especially for future space applications.

## Appendix A

## SAMPLE CALCULATIONS FOR KEVLAR MECHANISM'S RATE CONSTANTS

The photooxidation of Kevlar in $^{18}O_2$ is a second order reaction represented by equation

$$\text{Kevlar} + {}^{18}O_2 \longrightarrow \text{Products} \tag{A-1}$$

The rate constant $k_2$ of this bimolecular reaction (Equation A-1) becomes

$$k_2 = \frac{\ln \dfrac{[\text{Kevlar}][{}^{18}O_2]}{[\text{Kevlar}_0][{}^{18}O_2]}}{t([\text{Kevlar}_0] - [{}^{18}O_2])}$$

where $[\text{Kevlar}_0]$ and $[{}^{18}O_2]$ are the initial concentrations of Kevlar and $^{18}O_2$ in mole l$^{-1}$, respectively.

$$[\text{Kevlar}_0]_{^{46}CO_2} = \frac{1450 \text{ g/l}}{2 \times 119 \text{ g/mole}} = 6.1 \text{ mole/l}$$

$$[\text{Kevlar}_0]_{^{48}CO_2} = \frac{1450 \text{ g/l}}{119 \text{ g/mole}} = 12.2 \text{ mole/l}$$

where $[\text{Kevlar}_0]_{^{46}CO_2}$ and $[\text{Kevlar}_0]_{^{48}CO_2}$ are the initial concentrations of Kevlar to produce $^{46}CO_2$ and $^{48}CO_2$ products respectively. The consumption of one mole $^{18}O_2$ requires two moles of $+C_7H_5NO+$ moieties to produce two moles of $^{46}CO_2$. The density of Kevlar is 1450 g/l (1.45 g/cm$^3$) (Reference 4). When the Kevlar fabric was exposed to 100°C in 0.2 atm $^{18}O_2$ condition, the $^{18}O_2$ is assumed as an ideal gas to calculate $[{}^{18}O_2]$ in mole l$^{-1}$ at 100°C and 0.2 atm:

$$[{}^{18}O_2] = \frac{1 \text{ mole} \times 0.2 \text{ atm}}{373 \text{ K}/273 \text{ K} \times 22.4 \text{ l} \times 1 \text{ atm}} = 6.5 \times 10^{-3} \text{ mole/l}$$

After 30 minutes (1800 seconds) at 100°C in 0.2 atm $^{18}O_2$, the concentrations of $^{18}O_2$ and $+C_7H_5NO+$ moieties to produce $^{46}CO_2$ are $[^{18}O_2]_{^{46}CO_2}$ and $[\text{Kevlar}]_{^{46}CO_2}$, respectively:

$$[^{18}O_2]_{^{46}CO_2} = 6.53 \times 10^{-3} - 3.49 \times 10^{-3} \times 8.5 \times 10^{-4}$$

$$= 6.527 \times 10^{-3} \text{ mole/l}$$

where the $+C_7H_5NO+$ moieties in moles is $3.49 \times 10^{-3}$ and the mole ratio $[^{45}CO_2]/[+C_7H_5NO+]$ at 30 minutes is $8.5 \times 10^{-4}$ (Table 4, top figure), which is equivalent to the mole ratio of $^{18}O_2$ to $+C_7H_5NO+$ at 30 minutes for the photooxidation of Kevlar.

$$[\text{Kevlar}]_{^{46}CO_2} = 6.1 - \frac{3.49 \times 10^{-3}}{2} \times 8.5 \times 10^{-4} = 6.0999985 \text{ mole/l}$$

$$k_{2(^{46}CO_2)} = \frac{\ln \dfrac{6.0999985}{6.1} \times \dfrac{6.53 \times 10^{-3}}{6.527 \times 10^{-3}}}{1800\,(6.1 - 6.53 \times 10^{-3})} = 4.18 \times 10^{-8} \text{ l/sec/mole}$$

where $k_{2(^{46}CO_2)}$ is the rate constant of the photooxidation of Kevlar in $^{18}O_2$ atmosphere to produce $^{46}CO_2$ product.

After 30 minutes in 0.2 atm $^{18}O_2$, the concentrations of $^{18}O_2$ and $+C_7H_5NO+$ moieties to produce $^{48}CO_2$ are $[^{18}O_2]_{^{48}CO_2}$ $[\text{Kevlar}]_{^{48}CO_2}$, respectively:

$$[^{18}O_2]_{^{48}CO_2} = 6.53 \times 10^{-3} - 3.49 \times 10^{-3} \times 3.0 \times 10^{-6}$$

$$= 6.5299853 \times 10^{-3} \text{ mole/l}$$

where $+C_7H_5NO+$ moieties in moles is $3.49 \times 10^{-3}$ and the mole ratio $[^{48}CO_2]/[+C_7H_5NO+]$ at 30 minutes is $3.0 \times 10^{-6}$ (Table 3's third figure), which is equivalent to the mole ratio of $^{18}O_2$ to $+C_7H_5NO+$ at 30 minutes for the photooxidation of Kevlar.

$$[\text{Kevlar}]_{^{48}CO_2} = 12.2 - 3.49 \times 10^{-3} \times 3.0 \times 10^{-6} = 12.1999999895 \text{ mole/l}$$

$$k_{2(^{48}CO_2)} = \frac{\ln \dfrac{12.1999999895}{12.2} \times \dfrac{6.53 \times 10^{-3}}{6.5299853 \times 10^{-3}}}{1800\,(6.1 - 6.53 \times 10^{-3})} = 2.01 \times 10^{-10} \text{ l/sec/mole}$$

where $k_{2(^{48}CO_2)}$ is the rate constant of the photooxidation of Kevlar in $^{18}O_2$ atmosphere to produce $^{48}CO_2$ product.

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