

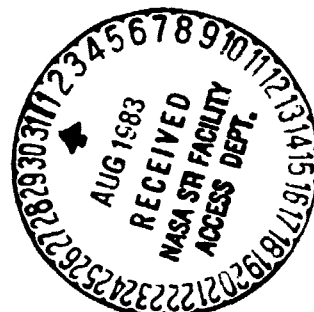
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Modeling of Photodegradation in Solar Cell Modules
of Substrate and Superstrate Design Made with
Ethylene-Vinyl Acetate as Pottant Material

ANNUAL REPORT

1981

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SUBSTRATE AND SUPERSTRATE DESIGN MADE WITH
ETHYLENE-VINYL ACETATE AS POTTANT MATERIAL
Annual Report (Toronto Univ.) 17 p

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A. C. Somersall and J. E. Guillet*

University of Toronto

* Principal Investigator

ABSTRACT

In the first year of this contract, a computer model was developed and demonstrated to simulate, in principle, the chemical changes in the photooxidation of hydrocarbons using as input data a set of elementary reactions, corresponding kinetic rate data and appropriate initial concentrations.

Early attempts to validate the fundamental kinetics and mechanisms with the experimental study of alkane photooxidation in our laboratory were abandoned during the past year when we proved that, at room temperature, the rates of hydrogen abstraction by peroxy radicals were too slow for significant oxidation of the alkane substrate to be important.

However, we were able to verify the numerical procedure, independent of our particular data base, by reproducing concentration-time profiles for a model reaction set describing the cesium flare system in the upper atmosphere. Our simulation was identical to that given in the literature. Experimental verification of our data base is to be attempted by weatherometry studies in the coming year.

Work on the new diagnostic techniques has been completed. Our adapted automated viscometer has been demonstrated to be an efficient and reliable tool for routine measurements of viscosity (molecular weight) changes in solid samples after batch solutions have been made up. The laser photolysis-GC method for monitoring extremely low levels of oxidation in polymers proved to be impractical because the yields of carbon monoxide were too low for quantification.

Much progress has been made with the computer model. The reaction matrix was completely revised, resulting in a new scheme of 31 reactions and corresponding rate data (see Appendix). Thus, simulations now show for the first time, lifetimes in excess of ten years. The results to date lead us to some tentative observations.

1. The photooxidation process has a long induction period of up to several years, followed by a rapid deterioration. To understand and control this early stage (induction) is crucial.
2. Chemical changes lead principally to the formation of alcohols, ketones and crosslinking which affect the physical properties.
3. The peroxy radicals dominate the chemistry so that the most appropriate stabilisation mechanism could probably be an efficient peroxy radical trap.
4. The rates of formation of major species show exponential behaviour as observed experimentally for polyethylene, right up to embrittlement.
5. Effects of initiator concentration, light intensity and diffusion have also been examined and preliminary results are qualitatively consistent with all our laboratory experience to date.

I. INTRODUCTION AND OBJECTIVES

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The JPL Flat-Plate Solar Array (FSA) Program has identified a number of possible configurations for modules containing silicon solar cells suitable for construction of a solar energy generating station and also for small-scale applications involving the use of solar-generated electricity. Although it appears possible now to meet many of the original design criteria for the cost of the components of these modules, a most critical feature of the design is that the components must maintain their integrity and function for a minimum efficiency equivalent to 20 years in an outdoor environment which features strong solar UV intensity.

To date, a number of failure and degradation modes have been identified. These include:

- | | |
|--------------------------------------|------------------------------------|
| 1. Soiling | 6. Electrical insulation breakdown |
| 2. Cell cracking/hot spots | 7. Encapsulant thermal degradation |
| 3. Interconnect fatigue | 8. ENCAPSULANT PHOTODEGRADATION |
| 4. Structural failure/glass breakage | 9. Delamination |
| 5. Electrical terminal failure | 10. Corrosion |

Any attempt to develop a technology for producing low-cost, long-life photovoltaic modules and arrays must therefore come to terms with the weathering effects experienced by the materials exposed to the sun's ultraviolet, oxygen, moisture and the stresses imposed by continuous thermal cycling, among other things. Polymeric substances which could find application as convenient protective covers, potting/adhesives and backcovers undergo slow, complex photo-oxidation which changes the chemical and physical properties of these materials. Absorption of the ultraviolet in the tail of the solar spectrum can cause the breaking of chemical bonds, resulting in embrittlement and increased permeability, or to crosslinking which can produce shrinking and cracks. In addition, oxidation often leads to discoloration and reduced transparency, and to the formation of polar groups which could affect electrical properties.

Much work has already been done to unravel the complexities of photo-oxidative processes and to develop some highly effective light (UV) stabilizers which can delay the onset of polymer embrittlement. A good review has been presented by Carlsson et al.¹ Some polymer systems have also been exploited to fabricate plastics with controlled lifetimes in the short range.^{2,3} However, very little is known about the ultimate changes that occur in polymeric substances after very long periods such as the 20-year regime appropriate for economic photovoltaic power plants.

There is no good way to predict the rates of the chemical and/or physical changes which occur from accelerated tests. In part, the problem has been that there is no adequate laboratory method to measure these effects over such

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extended times. Furthermore, accelerated tests (in which materials are exposed to higher intensity UV sources in controlled atmospheres) are of limited value in predicting rates since there is often no reciprocity between intensity and time of exposure.

A new procedure has been adopted in this work directed to developing for the first time, a reliable predictive capability for the lifetime of plastic components, particularly in solar energy modules. The procedure includes the following steps:

1. Identification of failure mechanisms of plastic components of the modules
2. Determination of the chemical or physical causes of these mechanisms
3. Development of precise analytical procedures to detect these chemical or physical changes at an early stage
4. Construction of a computer model using a series of elementary rate equations to describe the chemistry and physics of these changes
5. Validation of the mathematical model by comparison of data from real but well-defined accelerated photochemical systems
6. Prediction of actual performance lifetime by means of real-time monitoring of early degradation in appropriate outdoor locations and, using the computerised simulation, extrapolation to very much longer times

Other workers in the FSA project have done ranking studies to select optimal material systems which should have tolerable levels of degradation in 20-25 years and yet meet the other basic design criteria. Of the prime candidates selected as potential pollutant materials, an encapsulant grade of a copolymer of ethylene-vinyl acetate (EVA, trade name ELVAX, from DuPont) has emerged as a front runner beside the alternate poly(n-butyl acrylate) (PnBA). We have, therefore, selected EVA as the polymer for which this new predictive capability will be developed. However, the general method, once refined and demonstrated, should find wide application to a wide variety of synthetic materials where a large number of fundamental reactions gives rise eventually to macroscopic deterioration.

II. THE COMPUTER PROGRAM

Numerical methods for the solution of any large set of coupled differential equations have been developed. The particular method originally due to Gear⁴ has been applied by Allara and Edelson for the pyrolysis of alkanes⁵ and later by others^{6,7} for similar processes. Smog formation and detailed small-molecule photochemistry have also been studied by these numerical simulations.⁸ Semi-quantitative prediction has been possible in these cases. However, our work is the first attempt to simulate photooxidation kinetics in the case of polymers.

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The computer package necessary to generate concentration-time profiles from a mechanistic model of elementary reactions and rate data was completed in the first year. Further improvements have taken place this year, especially to extend the maximum number of integration steps and also the output capabilities for selected data. Some subroutines were rewritten for this purpose.

Our model now consists of a set of reactions (Table I) for the basic reaction sequence based on the now well established mechanism of hydrocarbon oxidation. Rate parameters have been assigned to these fundamental equations, based on our best estimates from the literature⁹ (Table I). A problem with such a simulation study is that the predicted rates will be only as reliable as the rate parameter data base employed. We anticipate continuous refinement of this data base in further work, especially since a number of techniques are available for performing the sensitivity analysis required to appreciate the relative importance of particular reactions and rate data.¹⁰

The modified program calculates by stepwise integration in real time the varying concentrations of chemical species formed during photooxidation. To validate our numerical procedure we employed the data base given for the cesium flare system and generated curves identical to those of Edelson¹¹ for the same system (Figure 1). The excellent agreement between predicted and actual rate curves shows that the program itself (irrespective of the data base) performs in a satisfactory manner.

III. MECHANISM OF PHOTOOXIDATION

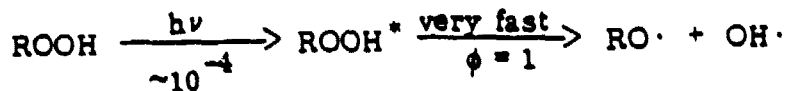
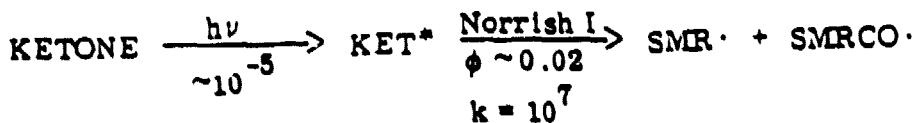
Amorphous Polyethylene

As a starting point for polymer photooxidation we have looked at a formal linear low-molecular-weight alkane (RH). In principle, this should be similar to amorphous high density polyethylene where short-range diffusion rates in reaction centres should approach that of viscous liquids. In practice, many polymers will show only chemical changes in the hydrocarbon moiety since bond breakage will commonly take place initially in the more labile C-H and C-C bonds. Initiation will take place following UV absorption by ketone or hydroperoxide groups or even fortuitously by some C-H bond cleavage. The possibilities of energy transfer among different groups have also been included in the model. Propagation takes place via the formation of peroxy radicals followed by hydrogen atom abstraction from the backbone and repeated fast oxygen addition. Peroxy radical chain carriers terminate by disproportionation to form alcohols and ketones. Further photolysis of ketone products leads to another autocatalytic chain.

Initiation

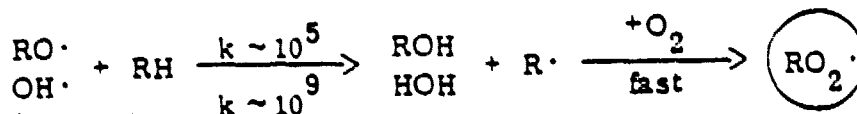
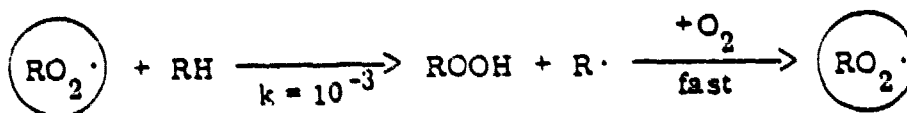


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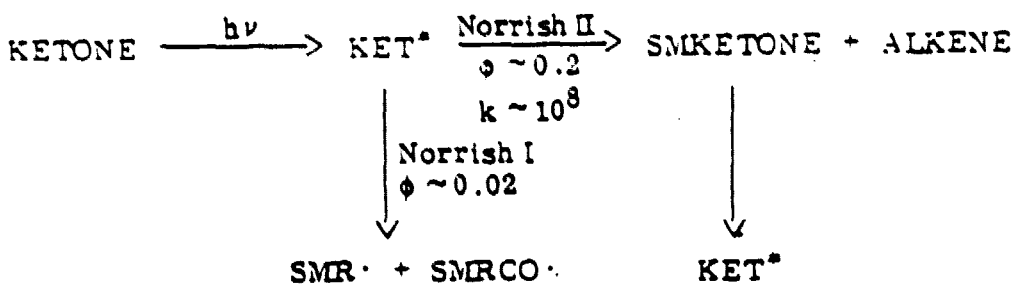


Propagation

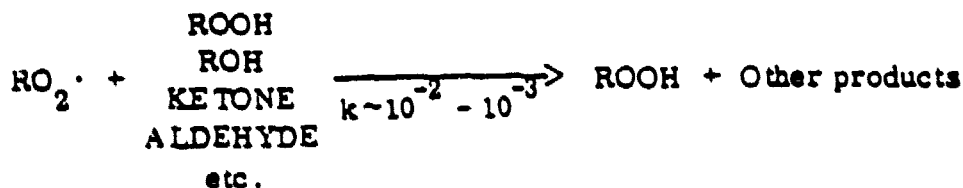
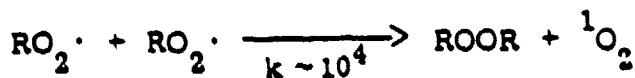
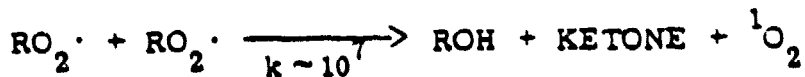
Peroxide chain



Ketone chain



Termination



The complete set of important reactions considered and the best literature estimates of corresponding rate constants have been summarised in Table I.

Ethylene-Vinyl Acetate Copolymer

Several studies have been carried out on the thermal degradation, ¹²⁻¹⁴ thermal oxidation^{15,16} and photooxidation¹⁷ of EVA.

EVA thermally degrades in two stages. Scission of acetoxy groups occurs at 275 to 350 °C in a manner similar to that of poly(vinyl acetate) (PVA) causing elimination of acetic acid and giving unsaturation by a molecular chain mechanism involving adjacent acetate units. The hydrocarbon chains of the polymer residue degrade above 400 °C. Thus, thermal decomposition of the acetate groups in EVA can be assumed to be negligible at room temperature.

Thermal oxidation of EVA occurs mainly in the PE segments following the usual autocatalytic radical mechanism analogous to that of polyethylene. The accompanying thermal degradation of the vinyl acetate units results in the evolution of acetic acid and generation of unsaturation as mentioned previously. Subsequent oxidation of the unsaturation was reported to produce various carbonyl-containing compounds including aldehydes, ketones, esters and acids. Again, it is apparent that thermal oxidation will be limited to the PE moiety at ambient temperatures.

The photooxidation of EVA has been reported only by Lugova et al.¹⁷ employing UV irradiation in air at room temperature. Their work suggests that the oxidation of the ethylene units and the photoreactions of the acetate chromophores proceed independently of each other, essentially in a parallel fashion.

The above results indicate that a generalized mechanism of photooxidation of EVA can be constructed using the known polyethylene photooxidation mechanism as a model for reactions expected to occur in the hydrocarbon portion of EVA. Similarly, information can be extracted from studies of the photooxidation of PVA and of acrylate polymers which allows formulation of the fundamental photochemical processes expected for the acetate groups in EVA. Some modifications to the present model for polyethylene will therefore be made in the coming year to allow for the differences due to substitution in EVA.

IV. PRELIMINARY RESULTS

Early computer modelling results have shown that the processes of photooxidation involve a long induction period, of up to several years in the pure hydrocarbon, followed by a fairly rapid deterioration (Figure 2). Initiation is effected fortuitously in the program by assigning a low rate constant for R-H cleavage or

TABLE I. Elementary Reactions in Polymer Photooxidation
and Corresponding Rates^a

	Reaction	Rate constant
1)	$RO_2^{\cdot} + RH \longrightarrow ROOH + RO_2^{\cdot}$	0.1×10^{-2}
2)	$RO_2^{\cdot} + RO_2^{\cdot} \longrightarrow ROH + \text{Ketone} + {}^1O_2$	0.2×10^8
3)	$RO_2^{\cdot} + ROH \longrightarrow ROOH + \text{Ketone} + HOO^{\cdot}$	0.5×10^{-1}
4)	$HOO^{\cdot} + RH \longrightarrow HOOH + RO_2^{\cdot}$	0.5×10^{-2}
5)	$HOO^{\cdot} + RO_2^{\cdot} \longrightarrow ROOH + {}^1O_2$	0.1×10^{10}
6)	$RO_2^{\cdot} + \text{Ketone} \longrightarrow ROOH + \text{Peroxy CO}$	0.5×10^{-2}
7)	$RO_2^{\cdot} + ROOH \longrightarrow ROOH + \text{Ketone} + OH^{\cdot}$	0.5×10^{-1}
8)	$RO_2^{\cdot} + \text{SMROH} \longrightarrow ROOH + \text{Aldehyde} + HOO^{\cdot}$	0.5×10^{-2}
9)	$RO_2^{\cdot} + \text{Aldehyde} \longrightarrow ROOH + \text{SMRCO}^{\cdot}$	0.1×10^3
10)	$OH^{\cdot} + RH \longrightarrow RO_2^{\cdot} + \text{Water}$	0.3×10^9
11)	$\text{Ketone} \xrightarrow{h\nu} \text{KET}^*$	0.3×10^{-5}
12)	$\text{SMKetone} \xrightarrow{h\nu} \text{KET}^*$	0.3×10^{-5}
13)	$\text{KET}^* \longrightarrow \text{SMRO}_2^{\cdot} + \text{SMRCO}^{\cdot}$	0.5×10^7
14)	$\text{SMRCO}^{\cdot} \longrightarrow \text{SMRO}_2^{\cdot} + \text{CO}$	0.5×10^6
15)	$\text{KET}^* \longrightarrow \text{Alkene} + \text{SMKetone}$	0.5×10^8
16)	$\text{KET}^* + O_2 \longrightarrow \text{Ketone} + {}^1O_2$	0.1×10^{10}
17)	$\text{KET}^* + ROOH \longrightarrow \text{Ketone} + RO^{\cdot} + OH^{\cdot}$	0.1×10^8
18)	$\text{KET}^* \longrightarrow \text{Ketone}$	0.1×10^{10}
19)	${}^1O_2 \longrightarrow O_2$	0.6×10^5

TABLE I (continued)

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	Reaction	Rate constant
20)	$^1\text{O}_2 + \text{Alkene} \longrightarrow \text{ROOH}$	0.1×10^4
21)	$\text{SMRO}_2^\cdot + \text{RH} \longrightarrow \text{SMROOH} + \text{RO}_2^\cdot$	0.1×10^{-2}
22)	$\text{SMROOH} \longrightarrow \text{SMRO}^\cdot + \text{OH}^\cdot$	0.3×10^{-4}
23)	$\text{SMRO}^\cdot + \text{RH} \longrightarrow \text{SMROH}$	0.1×10^6
24)	$\text{SMRCOO}^\cdot + \text{O}_2 \longrightarrow \text{SMRCOOO}^\cdot$	0.4×10^{10}
25)	$\text{SMRCOOO}^\cdot + \text{RH} \longrightarrow \text{SMRCOOOH} + \text{RO}_2^\cdot$	0.1×10^{-1}
26)	$\text{SMRCOOOH} \xrightarrow{h\nu} \text{SMRCO}_2^\cdot + \text{OH}^\cdot$	0.1×10^{-3}
27)	$\text{ROOH} \xrightarrow{h\nu} \text{RO}^\cdot + \text{OH}^\cdot$	0.3×10^{-4}
28)	$\text{RO}^\cdot \longrightarrow \text{SMRO}_2^\cdot + \text{Aldehyde}$	0.1×10^6
29)	$\text{RO}^\cdot + \text{RH} \longrightarrow \text{RO}_2^\cdot + \text{ROH}$	0.1×10^6
30)	$\text{SMRCO}_2^\cdot + \text{RH} \longrightarrow \text{Acid} + \text{RO}_2^\cdot$	0.1×10^6
31)	$\text{RO}_2^\cdot + \text{RO}_2^\cdot \longrightarrow \text{ROOR} + ^1\text{O}_2$	0.1×10^5

$\frac{a}{2} [\text{O}_2] = 10^{-3} \text{ M (constant); SMProduct = Product from chain cleavage.}$

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using low initial concentrations (ca. 10^{-5} M) for either ketone or hydroperoxide moieties. The principal products of photooxidation are ketones, alcohols, water and alkenes, with smaller quantities of aldehydes, acids, carbon monoxide, etc. (Table II).

The rates of formation of the major species show exponential behavior after the induction period is over (Figure 3). This conforms to the rate behavior for polyethylene observed experimentally in accelerated tests (Figure 4). An increase in the light intensity (reflected in a chosen systematic increase in all the photochemical absorption rates in the program) shows a systematic change in the exponential formation of ketone products (Figure 5) while the induction period is shortened (Figure 6). Increase in termination rate shortens the kinetic chain length and reduces the formation of product ketone. In this case, the exponential formation of ketone remains the same but is shifted in time to lengthen the induction period (Figure 7).

The autocatalytic process is initiated by a narrow concentration range of ketone initiator. At low levels ($<10^{-7}$ M) the induction period is excessively long for typical computer times and at high levels ($>10^{-3}$ M) the mutual termination of peroxy radicals is too fast to permit significant H-abstraction from the substrate.

These preliminary results are consistent with all of our experience to date of the photooxidation of ketone containing polymers.¹⁸

V. FUTURE WORK

Much work remains to be done in refinement of the model to allow for the inclusion of substituent groups, the reactivity of secondary and tertiary C-H bonds, the significance of diffusion, the influences of temperature cycling and dark reactions, and the impact of additives. In conclusion, we believe that these modelling studies which can simulate real systems (given reliable input data), represent a novel approach to the general understanding of polymer photooxidation phenomena which should lead to new understanding in the study of controlled lifetime for polymers and to the development of procedures which would allow the prediction of performance for plastics in solar applications.

TABLE II. Final Concentration Array.

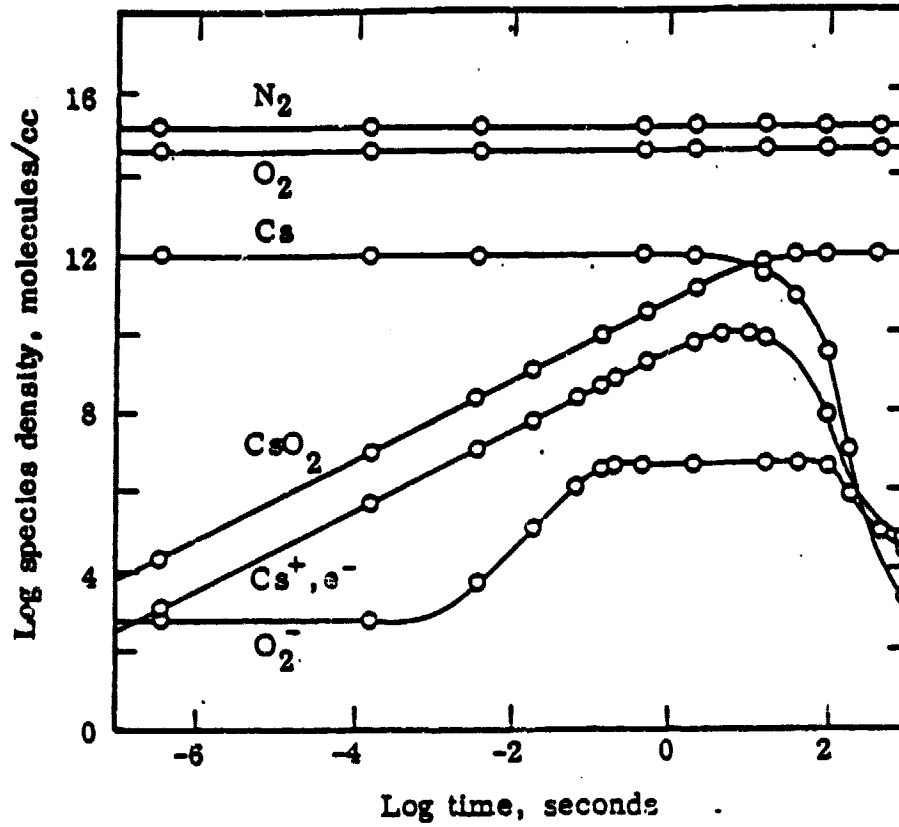
Time of Photooxidation, 10 Years

Species label	Initial conc., M	Final conc., M
RO ₂	--	0.25 x 10 ⁻⁷
RH	5.0	3.8
ROOH	--	0.77 x 10 ⁻⁴
ROH	--	0.49
Ketone	10 ⁻⁵	0.29
¹ O ₂	--	0.23 x 10 ⁻¹²
HOO	--	0.25 x 10 ⁻¹⁰
HOOH	--	0.21 x 10 ⁻⁴
Peroxy CO	--	0.89 x 10 ⁻³
OH	--	0.10 x 10 ⁻¹⁶
SMROH	--	0.19
Aldehyde	--	0.19 x 10 ⁻³
SMRCO	--	0.10 x 10 ⁻¹⁴
H ₂ O	--	0.40
KET*	--	0.88 x 10 ⁻¹⁵
SMKetone	--	0.14 x 10 ⁻¹
SMRO ₂	--	0.14 x 10 ⁻⁵
CO	--	0.19 x 10 ⁻¹
Alkene	--	0.16 x 10 ¹

TABLE II (continued)

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Species label	Initial conc., M	Final conc., M
ROOR	--	0.22×10^{-3}
RO	--	0.48×10^{-14}
SMROOH	--	0.18×10^{-3}
SMRO	--	0.14×10^{-13}
SMRCOOO	--	0.11×10^{-6}
SMRCOOOH	--	0.43×10^{-4}
SMR CO_2	--	0.11×10^{-13}
Acid	--	0.15



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FIGURE 1. Our numerical solutions for concentration vs. time profiles for the cesium flare (cf. ref. 10)

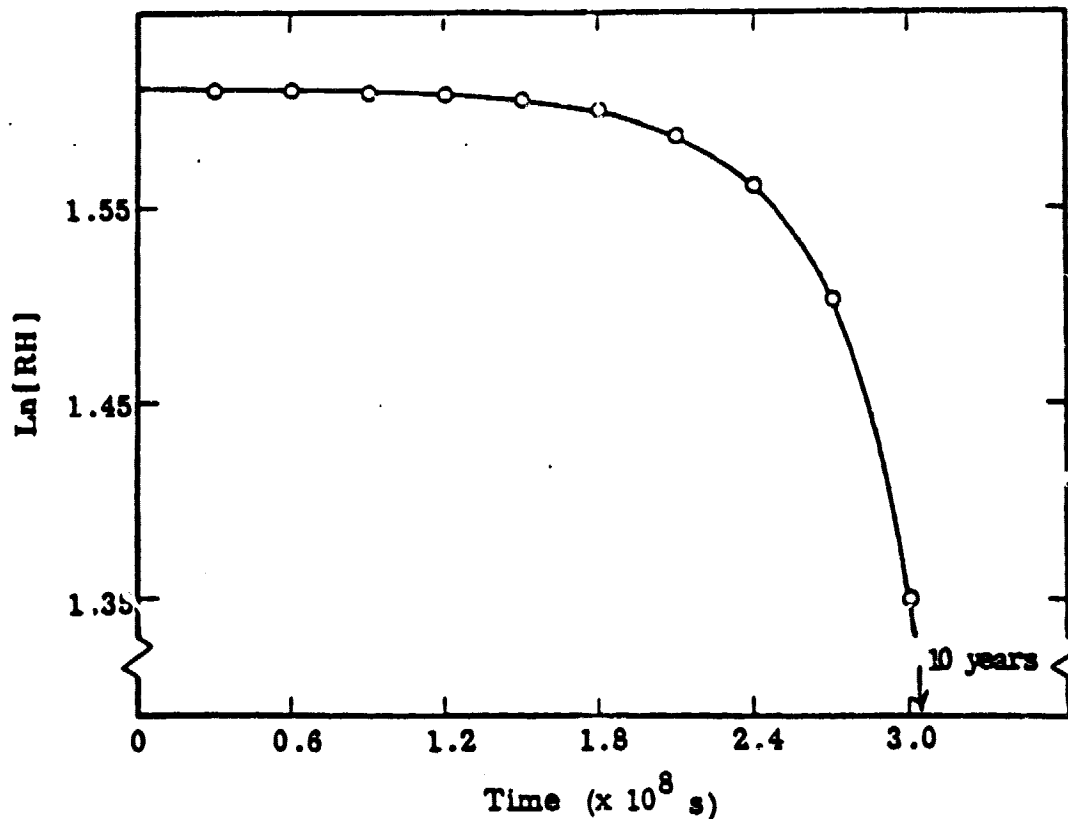


FIGURE 2. Photooxidation of linear alkanes (RH) vs. time.

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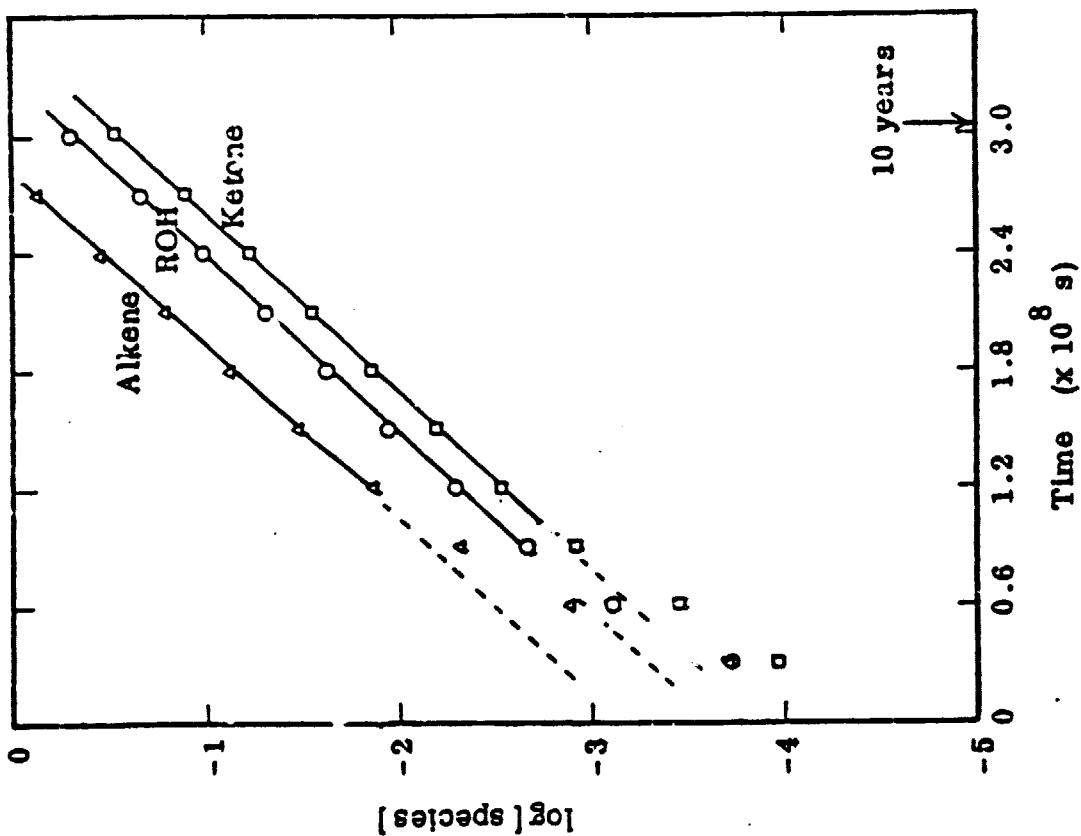


FIGURE 3. Variation of major product concentrations during photooxidation.

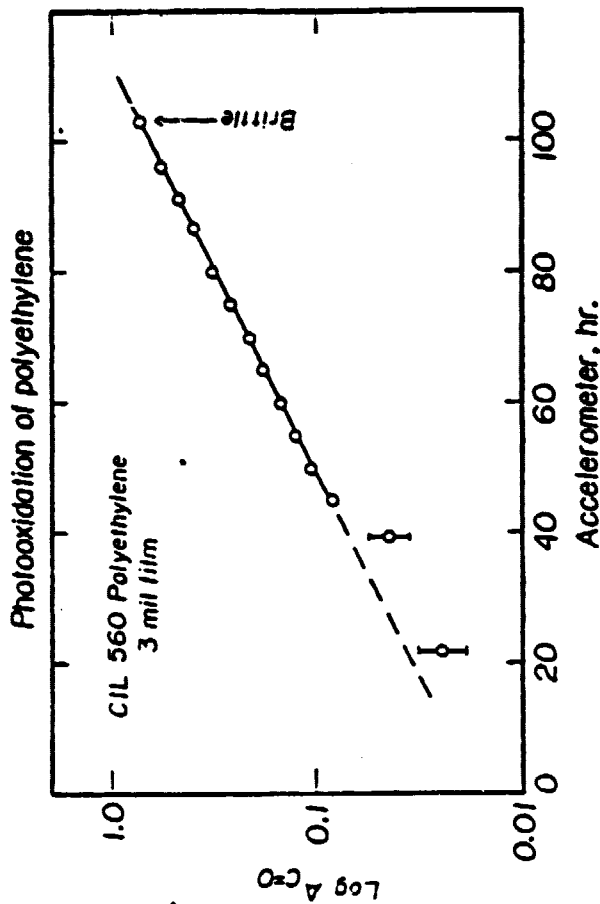


FIGURE 4. Photooxidation of polyethylene.

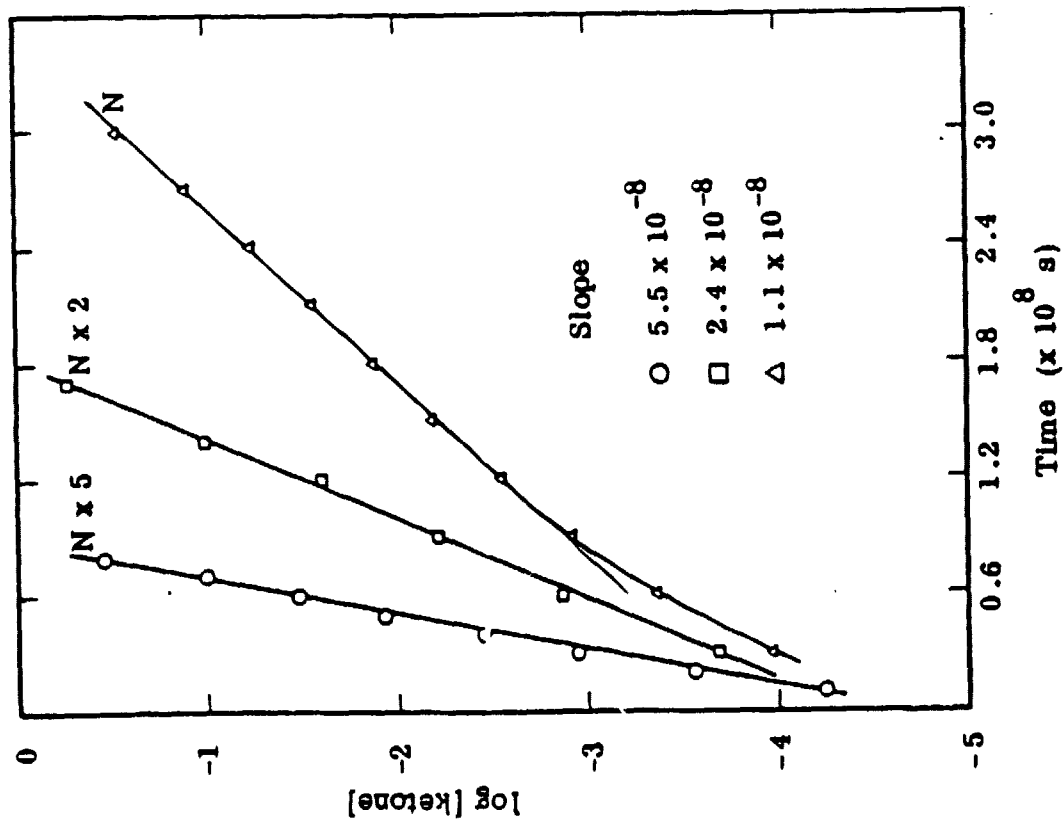


FIGURE 5. Effect of intensity on product formation during photooxidation.

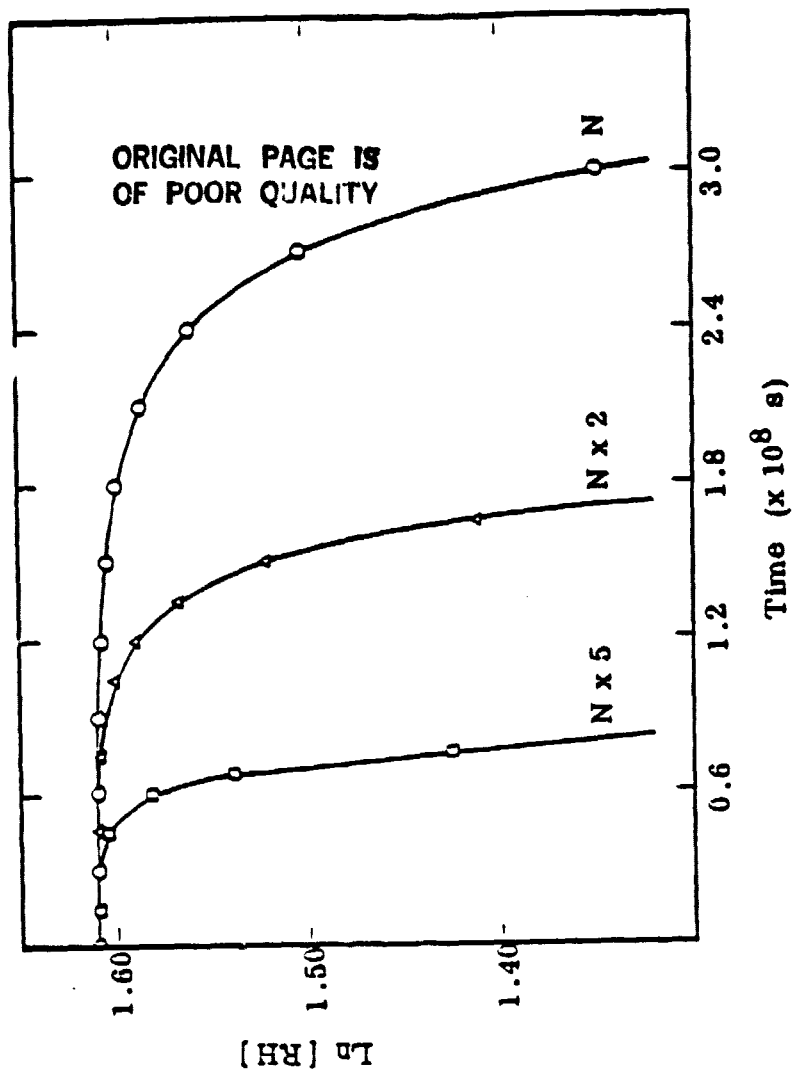


FIGURE 6. Photooxidation as a function of intensity of light.

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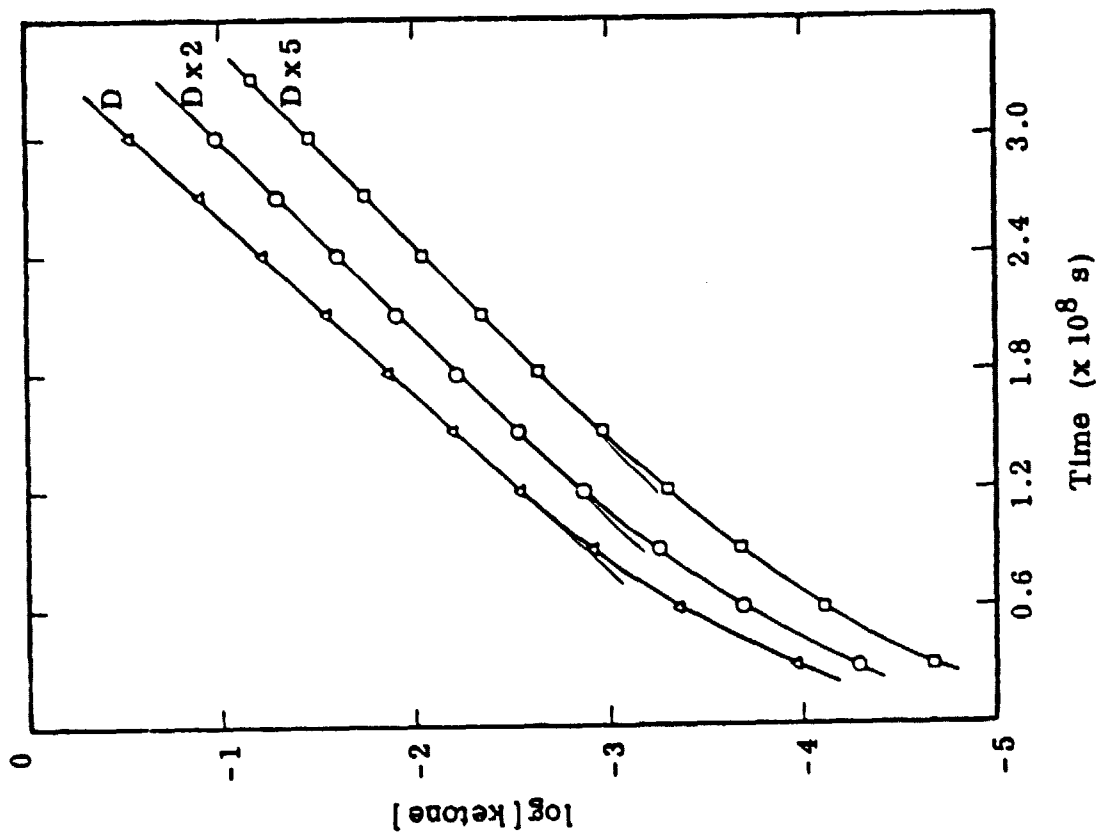


FIGURE 7. Effect of termination rate on product formation during photooxidation.

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