

N O T I C E

THIS DOCUMENT HAS BEEN REPRODUCED FROM
MICROFICHE. ALTHOUGH IT IS RECOGNIZED THAT
CERTAIN PORTIONS ARE ILLEGIBLE, IT IS BEING RELEASED
IN THE INTEREST OF MAKING AVAILABLE AS MUCH
INFORMATION AS POSSIBLE

**Modelling of Polymer Photodegradation
for Solar Cell Modules**

A Quarterly Technical Progress Report

Covering the Period April 1 - June 30, 1981

**(NASA-CR-165040) MODELLING OF POLYMER
PHOTODEGRADATION FOR SOLAR CELL MODULES
Quarterly Technical Progress Report, 1 Apr.
- 30 Jun. 1981 (Toronto Univ.) 16 p
HC A02/MF A01**

N82-14358

Unclas
08483

CSSL 07C G3/27

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

*** Principal Investigator**



Department of Chemistry, University of Toronto

Toronto, Canada M5S 1A1

LSA Project, Technology Development Area

Contract Goals and Objectives

As part of the Encapsulation Task, this research program is intended to model the photodegradation of synthetic polymers used as pottants and/or cover sheets in the LSA solar cell module designs. It involves the development of a computer simulation of the chemical processes that take place under weathering conditions which could, in principle, relate directly to the performance of these materials and afford some basis for predicting and/or controlling their useful lifetimes.

The program can be divided into three main parts:

1. The development of a computer program to model the weathering/ photooxidation of an ethylene-vinyl acetate copolymer as a typical candidate for LSA applications.
2. The development of new analytical procedures for the determination of photooxidation and photodegradation at early stages in solid polymer samples.
3. The development of weathering tests suitable for use with a computer kinetic model to provide a basis for extrapolated predictions.

"This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights."

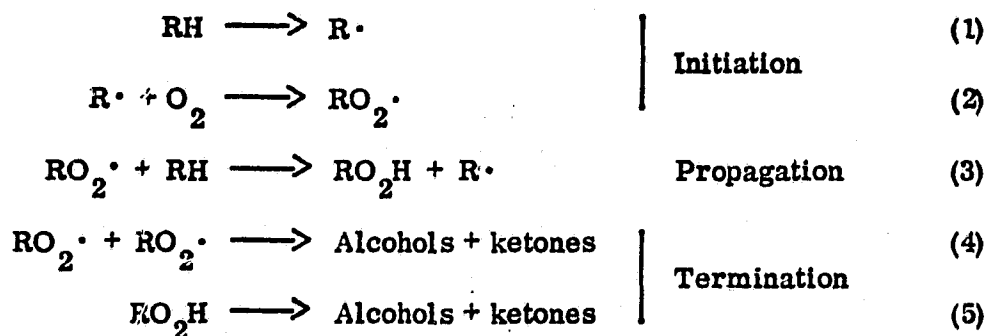
Summary

A computer program has been developed to calculate by numerical integration the varying concentrations of chemical species formed during photooxidation of a polymeric material over time, using as input data a choice set of elementary reactions, corresponding rate constants and a convenient set of starting conditions. Early attempts have been made to validate the proposed mechanism by experimentally monitoring the photooxidation products of small liquid alkanes which are useful starting models for ethylene segments of polymers like EVA.

During the second quarter of this year, there have been some major developments in our research program.

1. The Model

In earlier computer simulations we found that using our best set of elementary reactions and rates, the calculation would proceed through as many as 1000 iteration steps without any significant photooxidation of the alkanes (RH) taking place. We therefore arbitrarily increased the input rate constants for chain propagation (reaction 3) by several orders of magnitude and then we could observe extensive chemical change in the hydrocarbon:



Experimentally, we also observed very low yields of the isomeric ketones and alcohols. These tended to level off with time, indicating the absence of any significant chain mechanism. Following consultations with Dr. Keith

Ingold of the National Research Council of Canada, we now appreciate that at room temperature the rate of reaction (3) is so slow indeed that the termination step (reaction 4) dominates the photooxidation. Despite the ambiguity of reactions (4) and (5) predicting the same observed products, we conclude in effect, that the products we have been separating during the photooxidation of the liquid alkanes have been the products of photooxidation of the ketone and/or peroxide initiators, with minimal alkane solvent derivatives formed at best in extremely short chain lengths. It is not surprising then that such high concentrations (up to 10%) of initiator were necessary to observe significant amounts of product in days of irradiation with a medium pressure mercury lamp. The absorption of the initiators is very low at 313 nm so the product yields were correspondingly low, since no chain process was effectively initiated.

We therefore conclude that this model system has now proved inappropriate for our purposes and intend to use a different one in the future. A much better model system to validate any simulation of photooxidation might be the Ecolyte system. This is a patented formulation developed in Professor Guillet's laboratories, consisting of mixtures of small amounts of ketone-containing polymers blended with other commercial polymers in such a way as to afford programmed lifetimes for the resulting materials which we now can attempt to simulate.

2. The Method

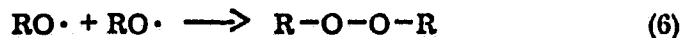
Another major problem we have been facing is the short oxidation times observed in the computer output. Typical results showed oxidation in a few days at most. When we reduced the propagation rate to lengthen the lifetime of the alkane, the integration procedure was completed without any significant oxidation. Yet, what we really would like to generate is behaviour over 10 to 20 years. This raised the question of the adequacy of the method: could the program really integrate over several years or is there an inherent limitation (such as the accuracy limitation to the maximum size of the step length)? The method has now been shown to be adequate.

We have taken two steps. First, we have completely revised the elementary reaction matrix, with some consultation from Dr. Ingold again, resulting in a new scheme of 31 or 32 reactions (see Appendix). This set is somewhat incomplete for EVA since no allowance is made for the different secondary and tertiary C-H groups and no corrections are included for the restricted diffusion of polymeric radicals in the solid state. Secondly, we have gained operational control of our integration parameters to increase the flexibility with the program.

The result is that without any arbitrary adjustment to the reaction rates, the computer simulation now shows for the first time lifetimes in excess of ten years when initiated by very small amounts of ketone, peroxide or some fortuitous alkyl radical-generating step (see Appendix).

Our 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.
2. The chemical changes that result lead to
 - (a) The formation of alcohols with polar -OH groups which could affect wettability and electrical resistance of the polymers.
 - (b) The formation of ketones which could become conjugated, leading to discoloration and which could also lead to scission and small molecule fragments, and
 - (c) Crosslinking through alkoxy radicals in a cage coupling to form peroxide linkages.



This crosslinking could cause the polymer to shrink and hence tear or pull away from connections and supports in a module failure mode.

3. The most appropriate stabilisation mechanism would probably be an efficient peroxy radical trap since it appears that the peroxy radicals dominate the chemistry.

Appendix

Some Examples of Input-Output Data Used in the Current Simulation Routine for Alkane Photooxidation

(N.B. A new plotting subroutine has been interfaced to provide more convenient graphs for the output of the concentration-time profiles.)

1	2	RO2	+ RH	-> ROOH	+ RO2	
2	3	RO2	+ RO2	-> ROH	+ KETONE	+ SO2
3	4	RO2	+ ROH	-> ROOH	+ KETONE	+ HCO
4	5	HOH	+ RH	-> HOOH	+ RO2	
5	6	HCO	+ RO2	-> ROOH	+ SO2	
6	7	RO2	+ KETONE	-> ROOH	+ PEROXYCO	
7	8	RO2	+ ROOH	-> ROOR	+ KETONE	+ OH
8	9	RO2	+ SMROH	-> ROOH	+ ALDEHYDE	+ HOH
9	10	RO2	+ ALDEHYDE	-> ROOH	+ SMRCO	
10	11	OH	+ RH	-> RO2	+ WATER	
11	12		KETONE	-> KET*		
12	13		SMKETONE	-> KET*		
13	14		KET*	-> SMRO2	+ SMRCO	
14	15		KET*	-> SMRO2	+ CO	
15	16		KET*	-> ALKENE	+ SMKETONE	
16	17	KET*	+ O2	-> KETONE	+ SO2	
17	18	KET*	+ ROOH	-> KETONE	+ RO	+ CH
18	19		KET*	-> KETONE		
19	20		SO2	-> O2		
20	21	SO2	+ ALKENE	-> ROOH		
21	22	SMRO2	+ RH	-> SMROOH	+ RO2	
22	23		SMROOH	-> SMRO	+ OH	
23	24	SMRO	+ RH	-> SMROH		
24	25	SMRCO	+ O2	-> SMRCOOO		
25	26	SMRCOOO	+ RH	-> SMRCOOOH	+ RO2	
26	27		SMRCOOOH	-> SMRCO2	+ OH	
27	28		ROH	-> RO	+ OH	
28	29		RO	-> SMRO2	+ ALDEHYDE	
29	30	RO	+ RH	-> RO2	+ ROH	
30	31	SMRCO2	+ RH	-> ACID	+ RO2	
31	32	RO2	+ RO2	-> ROOR	+ O2	

ORIGINAL PAGE IS
OF POOR QUALITY

INITIAL CONCENTRATION DATA (MOLES/L)

*****VARIABLE SPECIES*****CONCENTRATION*****

Variable Species	Concentration
1 RO2	0.0
2 RH	0.50000D+01
3 ROOH	0.0
4 ROH	0.0
5 KETONE	0.10000D-11
6 SO2	0.0
7 HO2	0.0
8 HOOH	0.0
9 PEROXYCO	0.0
10 OH	0.0
11 SMROH	0.0
12 ALDEHYDE	0.0
13 SMRCO	0.0
14 WATER	0.0
15 KET*	0.0
16 SMKETONE	0.0
17 SMRU2	0.0
18 CO	0.0
19 ALKENE	0.0
20 ROOR	0.0
21 RO	0.0
22 SMROOH	0.0
23 SMRO	0.0
24 SMRCOOO	0.0
25 SMRCOOOH	0.0
26 SMRCO2	0.0
27 ACID	0.0

*****CONSTANT SPECIES*****CONCENTRATION*****

Constant Species	Concentration
28 O2	0.10000D-02

ORIGINAL PAGE IS
OF POOR QUALITY

REACTION RATE CONSTANTS...TEMP=300.0 K...

AXN LABEL	RATE CONSTANT	PRE-EXP FACTOR
1 2	0.100000-02	
2 3	0.200000+05	
3 4	0.500000-01	
4 5	0.500000-02	
5 6	0.100000+10	
6 7	0.500000-02	
7 8	0.500000-01	
8 9	0.500000-02	
9 10	0.100000+03	
10 11	0.300000+09	
11 12	0.300000-05	
12 13	0.300000-05	
13 14	0.500000+07	
14 15	0.500000+06	
15 16	0.500000+08	
16 17	0.100000+10	
17 18	0.100000+08	
18 19	0.100000+10	
19 20	0.200000+05	
20 21	0.100000+04	
21 22	0.100000-02	
22 23	0.300000-04	
23 24	0.100000+06	
24 25	0.400000+10	
25 26	0.100000-01	
26 27	0.100000-02	
27 28	0.300000-04	
28 29	0.100000+06	
29 30	0.100000+06	
30 31	0.100000+06	
31 32	0.100000+05	

***INTEGRATION REQUESTED--STARTING INTEGRATION PARAMETER

ITEM	VALU
INTEGRATION TIME LIMITS--STARTING TIME	0.0

ORIGINAL PAGE IS
OF POOR QUALITY

INTEGRATION REQUESTED--STARTING INTEGRATION PARAMETERS FOLLOW

ITEM	VALUE
INTEGRATION TIME LIMITS--STARTING TIME	0.0 SEC
--STOPPING TIME	0.10000000D+10 SEC
TIME STEP LENGTH--MINIMUM	0.10D-24 SEC
--INITIAL	0.10D-14 SEC
EQUAL TIME DATA STORAGE LIMIT	100 DATA SETS
MAXIMUM NUMBER OF INTEGRATION STEPS	1000 ITERATIONS
MAXIMUM CPU TIME LIMIT	0.5 MIN
REQUESTED ERROR TOLERANCE	0.10D-04 PER STEP

***INTEGRATION MODE -- CHORD METHOD USING FULL ANALYTIC JACOBIAN ANAL
-- GEAR STIFF METHODS EMPLOYED

ORIGINAL PAGE IS
OF POOR QUALITY

-->STARTING TIME

TOTAL TIME= 0.0 SEC

-->STOPPING TIME

TOTAL TIME= 0.251109300+09 SEC = 2907 DAYS, 6 HOURS, 48 MIN

SPECIES INDEX	SPECIES LABEL	INITIAL CONC (M/L)	FINAL CONC (M/L)
1	NO2	0.0	0.14242230-07
2	RH	0.50000000D+01	0.46062620D+01
3	ROOH	0.0	0.149223850-04
4	ROH	0.0	0.167633720+00
5	KETONE	0.100000000-11	0.961122350-01
6	SO2	0.0	0.755237530-13
7	HOC	0.0	0.868134620-11
8	HOCH	0.0	0.804602970-05
9	PEROXY	0.0	0.176419910-03
10	OH	0.0	0.261618510-17
11	SMRCH	0.0	0.627044000-01
12	ALDEHYDE	0.0	0.574980200-04
13	SMRCO	0.0	0.378670480-15
14	WATER	0.0	0.135441320+00
15	KET*	0.0	0.286348830-15
16	SMKETONE	0.0	0.473029000-02
17	SMRO2	0.0	0.359243070-06
18	CO	0.0	0.547789730-02
19	ALKENE	0.0	0.547008640+00
20	ROOR	0.0	0.790857430-04
21	RO	0.0	0.795596640-15
22	SMROOH	0.0	0.551086720-04
23	SMRO	0.0	0.355915740-14
24	SMRCOO	0.0	0.328830770-07
25	SMRCOOH	0.0	0.151426520-04
26	SMRCO2	0.0	0.328740600-14
27	ACID	0.0	0.574333330-01

***UTCC GOULD 5200 PLOT SOFTWARE, VERSION 52 LEVEL 1, AUGUST 1977.

PLOTST COMPLETED; NAME IS: SIMULATN

FIG. 1

SPECIES RH

CALC. DATA

EXPTL. DATA

1. RH

o

ORIGINAL PAGE IS
OF POOR QUALITY

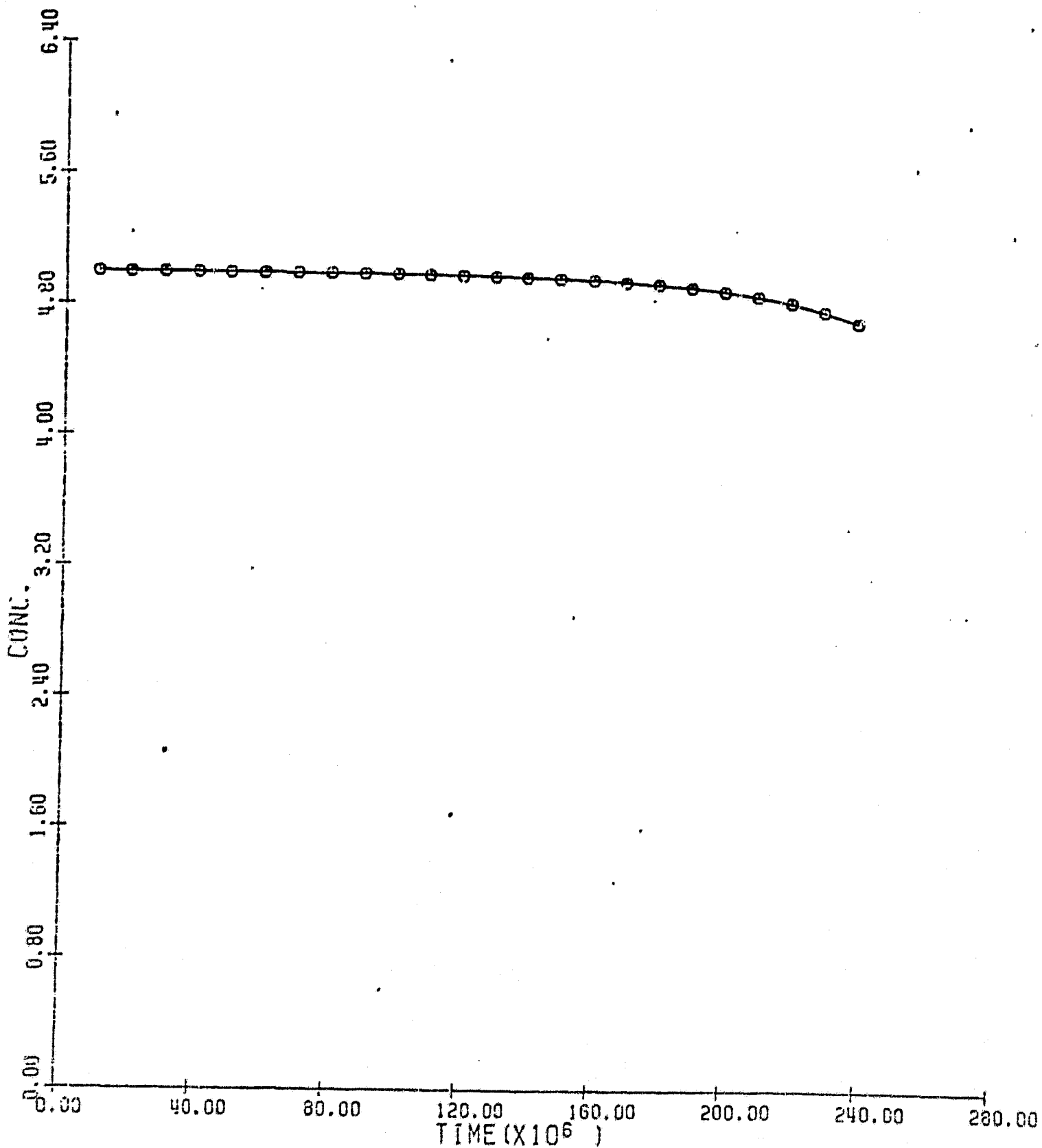


FIG. 2

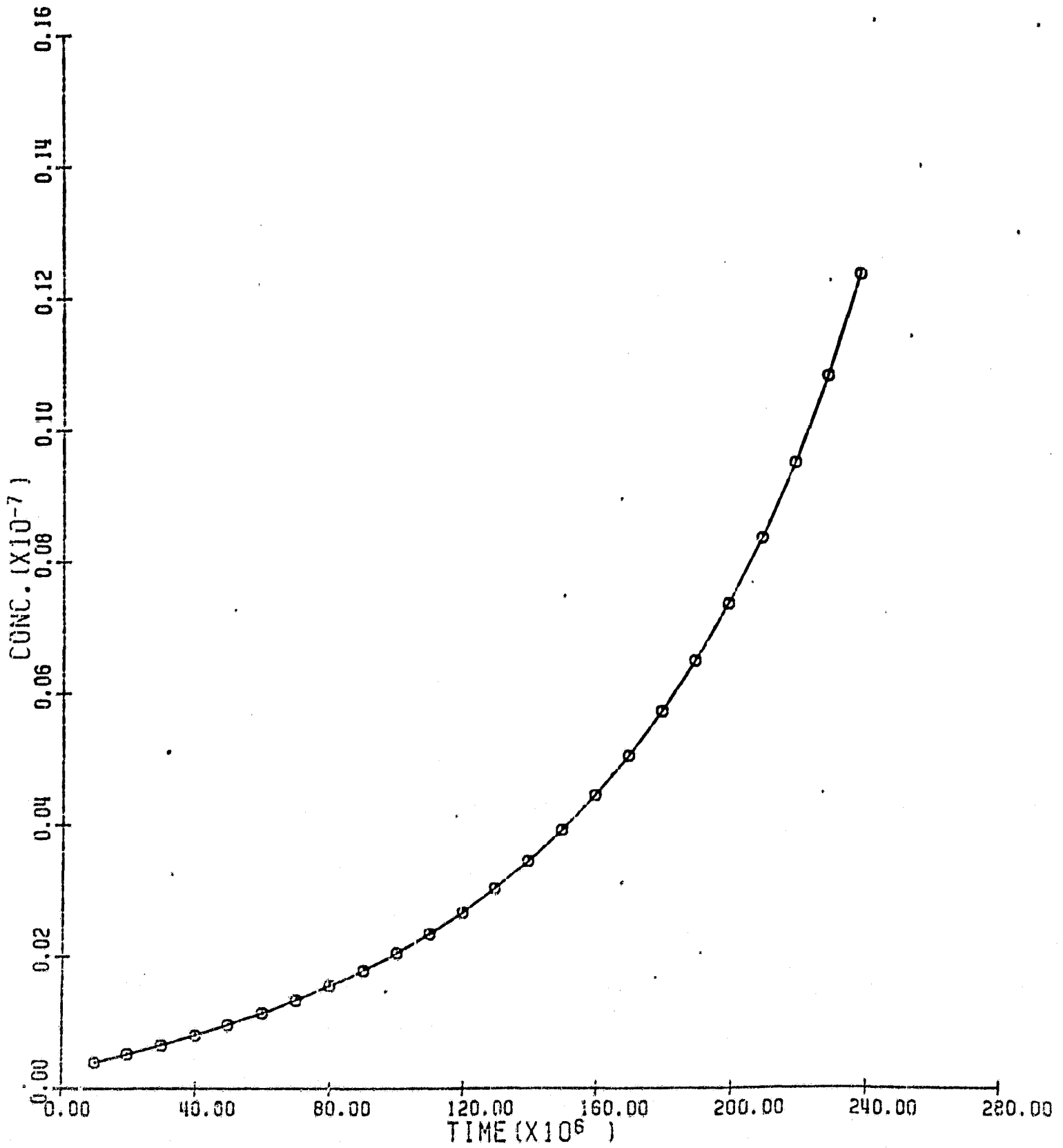
SPECIES NO2

CALC. DATA

EXPTL. DATA

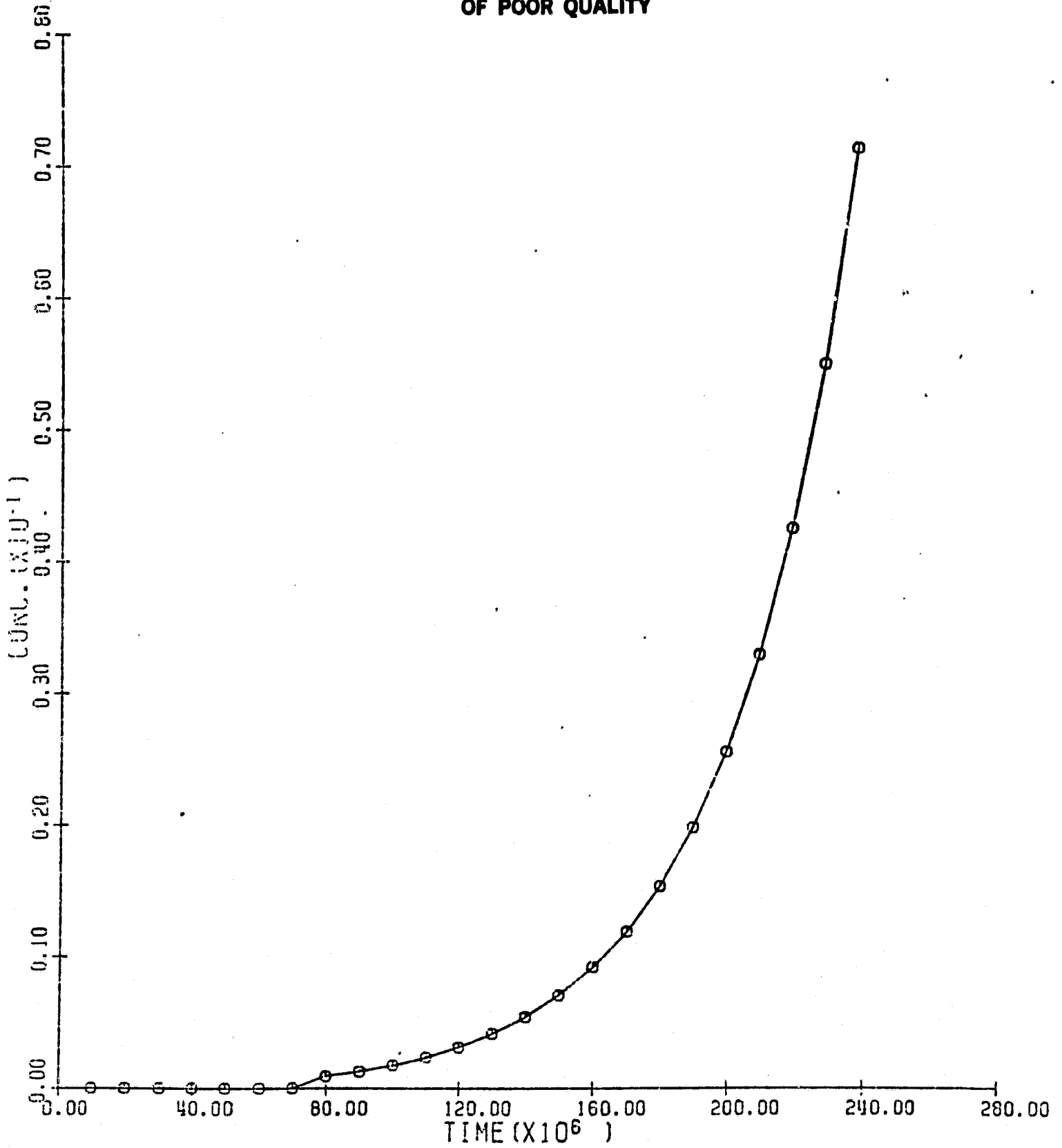
J. NO2

o



1. KETONE ○

ORIGINAL PAGE IS
OF POOR QUALITY

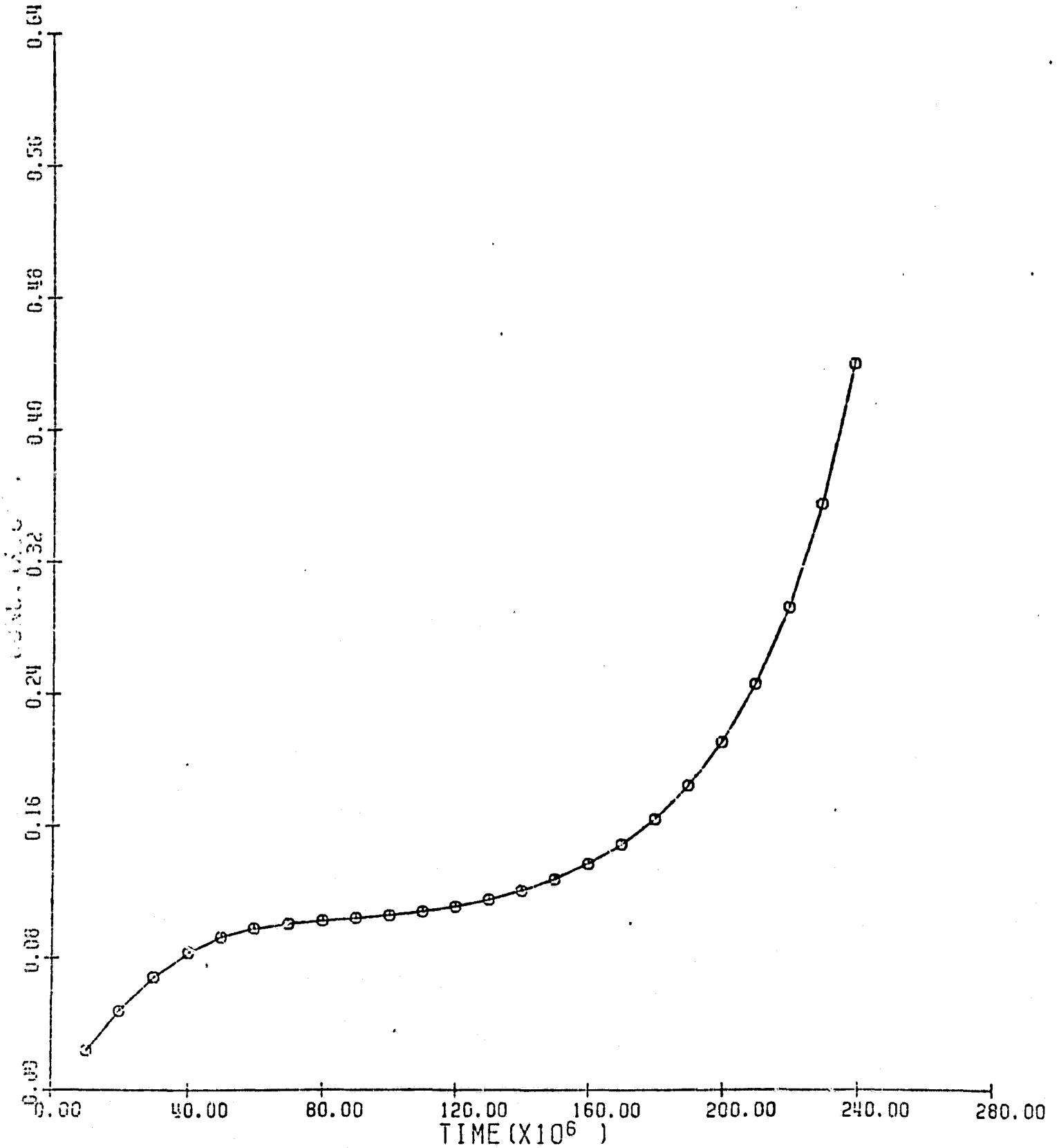


CALC. DATA

EXPTL. DATA

1. ALDEHYDE ○

ORIGINAL PAGE IS
OF POOR QUALITY



1.00H

0

ORIGINAL PAGE IS
OF POOR QUALITY

