N87-16437

COMPUTER MODELING OF PHOTODEGRADATION

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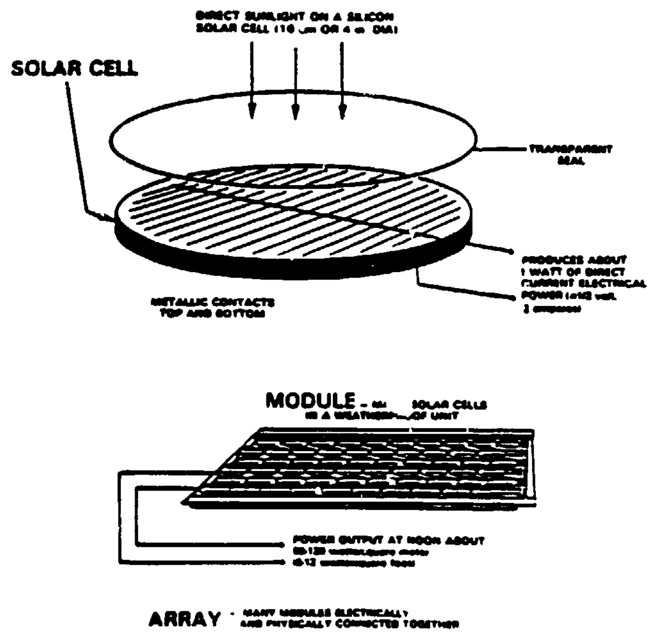
Construction and Operation of Solar Cells, Modules, and Arrays



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Chemical Weathering Factors

- *SOLAR (UV) CYCLE*
- *TEMPERATURE CYCLES*
- *OXYGEN*
- *MOISTURE*
- *POLYMER COMPOSITION*
  - *STRUCTURE*
  - *FORMULATION*
  - *IMPURITIES*
  - *ADDITIVES*

Chemical Weathering Effects

MOLECULAR WEIGHT CHANGES

Scission: *Embrittlement*
Permeability

Crosslinks: *Shrinking*
Wrinkles

PHOTOTHERMAL OXIDATION

Unsaturation: *Discoloration*
Transparency

Polar groups: *Electrical properties*
Wettability

Computer Simulation

INPUT
- *Mechanism (rates)*
- *Conditions*
- *Integration parameter*

INTERFACE
- *Block of ordinary differential equations*

SOLUTION
- *Numerical integration*
  - STIFF · GEAR

OUTPUT
- *Concentration vs. time*
  - *10-20 years*

Starting Conditions

SUBSTRATE	RH (cf. amorphous linear PE)	
INITIATORS	Ketone	10^{-3} M
	Hydroperoxide	
	Fortuitous	
OXYGEN	Constant	10^{-3} M
TEMPERATURE	Ambient	
RATES	Literature (cf. fluid)	
SOURCE	Daylight	

The Mechanism: A Model of 51 Elementary Reactions

INITIATION

$$RH \xrightarrow{?} R\cdot$$

$$R-\overset{O}{\overset{\|}{C}}-R \xrightarrow{h\nu} R-\overset{O}{\overset{\|}{C}}\cdot \quad R\cdot$$

$$R-O-O-H \xrightarrow[\Delta]{h\nu} R-O\cdot \quad \cdot O-R$$

PROPAGATION

$$R\cdot \xrightarrow{O_2} RO_2^{\cdot}$$

$$RO_2^{\cdot} + RH \longrightarrow ROOH + R\cdot$$

$$ROOH \longrightarrow RO\cdot + OH\cdot$$

$$OH\cdot + RH \longrightarrow HOH + R\cdot$$

$$RO\cdot + RH \longrightarrow ROH + R\cdot$$

TERMINATION

$$RO_2^{\cdot} - RO_2^{\cdot} \longrightarrow RO \longrightarrow \text{Alcohol}$$

$$\downarrow$$

$$R-O-O-R \quad \text{(Crosslink)}$$

$$RO_2^{\cdot} - RO_2^{\cdot} \longrightarrow \text{Ketone} \xrightarrow{h\nu} \text{Scission}$$

Table 1. Data Set: Photooxidation Reaction Scheme and Activation Parameters

	Reaction matrix			A	E kcal/mol
1.	Ketone	⟶	KET*	0.70×10^{-9}	0
2.	KET*	⟶	$SMRO_2$ + SMRCO	0.59×10^{9}	4.8
3.	SMRCO	⟶	$SMRO_2$ + CO	0.80×10^{17}	15
4.	KET*	⟶	Alkene + SMKetone	0.56×10^{8}	2.0
5.	SMKetone	⟶	SMKET*	0.70×10^{-9}	0
6.	SMKET*	⟶	$SMRO_2$ + CH_3CO	0.32×10^{13}	8.5
7.	SMKET*	⟶	Alkene + Acetone	0.56×10^{9}	2.0
8.	ROOH	⟶	RO + OH	0.13×10^{9}	0
9.	RO_2 + RH	⟶	ROOH + RO_2	0.10×10^{10}	17.0
10.	$SMRO_2$ + RH	⟶	SMROOH + RO_2	0.10×10^{10}	17.0
11.	SMROOH	⟶	SMRO + OH	0.13×10^{-9}	0
12	SMRO + RH	⟶	SMROH + RO_2	0.16×10^{10}	6.2
13.	RO + RH	⟶	ROH + RO_2	0.16×10^{10}	6.2
14.	RO	⟶	$SMRO_2$ + Aldehyde	0.32×10^{16}	17.4
15.	KET* + ROOH	⟶	Ketone + RO + OH	0.25×10^{10}	11.6
16.	SMKET* + ROOH	⟶	SMKetone + RO + OH	0.25×10^{10}	11.6
17.	SMRCO + O_2	⟶	SMRCOOO	0.80×10^{14}	9.6
18.	SMRCO + RH	⟶	RO_2 + Aldehyde	0.10×10^{10}	7.3
19.	SMRCOOO + RH	⟶	SMRCOOOH + RO_2	0.10×10^{10}	17.0
20.	SMRCOOOH	⟶	SMRCOO + OH	0.13×10^{-9}	0
21.	SMRCOO	⟶	$SMRO_2$ + CO_2	0.10×10^{15}	6.6

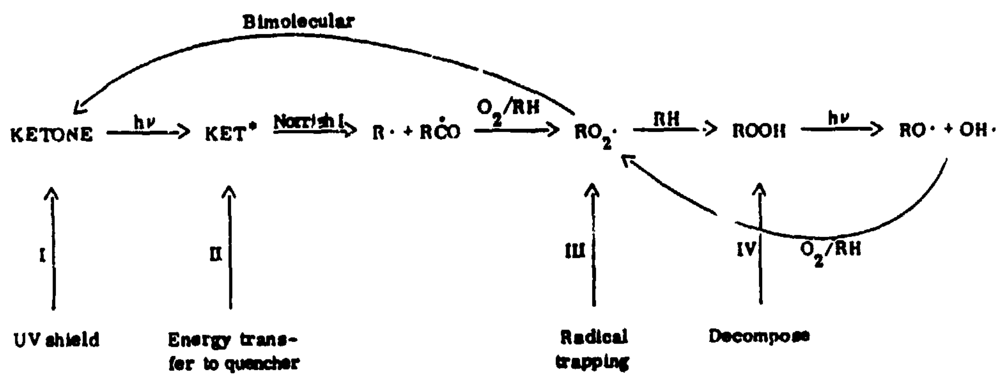
Table 1. (Cont'd)

22.	SMRCOO + RH	$\longrightarrow$	Acid + RO_2	0.10×10^{10}	17.0
23.	OH + RH	$\longrightarrow$	RO_2 + Water	0.10×10^{10}	0.5
24.	CH_3CO + RH	$\longrightarrow$	RO_2 + CH_3CHO	0.10×10^{10}	7.3
25.	CH_3CO + O_2	$\longrightarrow$	CH_3COOO	0.89×10^{14}	9.6
26.	CH_3COOO + RH	$\longrightarrow$	CH_3COOOH + RO_2	0.10×10^{10}	17.0
27.	CH_3COOOH	$\longrightarrow$	CH_3COO + OH	0.13×10^{-9}	0
28.	CH_3COO + RH	$\longrightarrow$	CH_3COOH + RO_2	0.10×10^{15}	6.6
29.	KET*	$\longrightarrow$	Ketone	0.10×10^{9}	0
30.	SMKET*	$\longrightarrow$	SMKetone	0.10×10^{9}	0
31.	KET* + O_2	$\longrightarrow$	Ketone + SO_2	0.89×10^{14}	9.6
32.	SMKET* + O_2	$\longrightarrow$	SMKetone + SO_2	0.89×10^{14}	9.6
33.	RO_2 + RO_2	$\longrightarrow$	ROH + Ketone + SO_2	0.25×10^{10}	11.6
34.	RO_2 + ROH	$\longrightarrow$	ROOH + Ketone + HOO	0.10×10^{10}	15.3
35.	HOO + RH	$\longrightarrow$	HOOH + RO_2	0.32×10^{9}	15.0
36.	HOO + RO_2	$\longrightarrow$	ROOH + SO_2	0.32×10^{9}	2.1
37.	RO_2 + Ketone	$\longrightarrow$	ROOH + Peroxy CO	0.13×10^{5}	8.9
38.	Peroxy CO + RH	$\longrightarrow$	PER OOH + RO_2	0.10×10^{10}	17.0
39.	PER OOH	$\longrightarrow$	PER O + OH	0.13×10^{-9}	0
40.	[illegible]RO + RO_2	$\longrightarrow$	DIKetone + ROOH	0.25×10^{10}	11.6
41.	RO_2 + ROOH	$\longrightarrow$	ROOH + Ketone + OH	0.25×10^{8}	11.6
42.	RO_2 + SMROH	$\longrightarrow$	ROOH + Aldehyde + HOO	0.10×10^{10}	15.3
43.	RO_2 + Aldehyde	$\longrightarrow$	ROOH + SMRCO	0.25×10^{10}	11.6
44.	RO_2 + RO_2	$\longrightarrow$	ROOR + SO_2	0.33×10^{12}	16.0

Table 1. (Cont'd)

45.	SO_2	$\longrightarrow$	O_2	0.63×10^{5}	0
46.	SO_2 + Alkene	$\longrightarrow$	ROOH	0.20×10^{14}	10.0
47.	RO_2 + Alkene	$\longrightarrow$	Branch	0.16×10^{9}	11.6
48.	$SMRO_2$ + Alkene	$\longrightarrow$	ROOH	0.16×10^{9}	11.6
49.	RO_2 + QH	$\longrightarrow$	ROOH + Q	0.16×10^{8}	5.2
50.	KET* + Q1	$\longrightarrow$	Ketone + Heat	0.80×10^{13}	[illegible]
51.	ROOH + QD	$\longrightarrow$	PRODS	0.80×10^{13}	9.5
52.	ROOH	$\longrightarrow$	RO· + OH·	0.63×10^{15}	35
53.	SMROOH	$\longrightarrow$	SMRO + OH	0.63×10^{15}	35
54.	SMRCOOOH	$\longrightarrow$	SMRCOO + OH	0.63×10^{15}	35
55.	CH_3COOOH	$\longrightarrow$	CH_3COO + OH	0.63×10^{15}	35
56.	PEROOH	$\longrightarrow$	PERO + OH	0.53×10^{15}	35

Stabilization Mechanisms

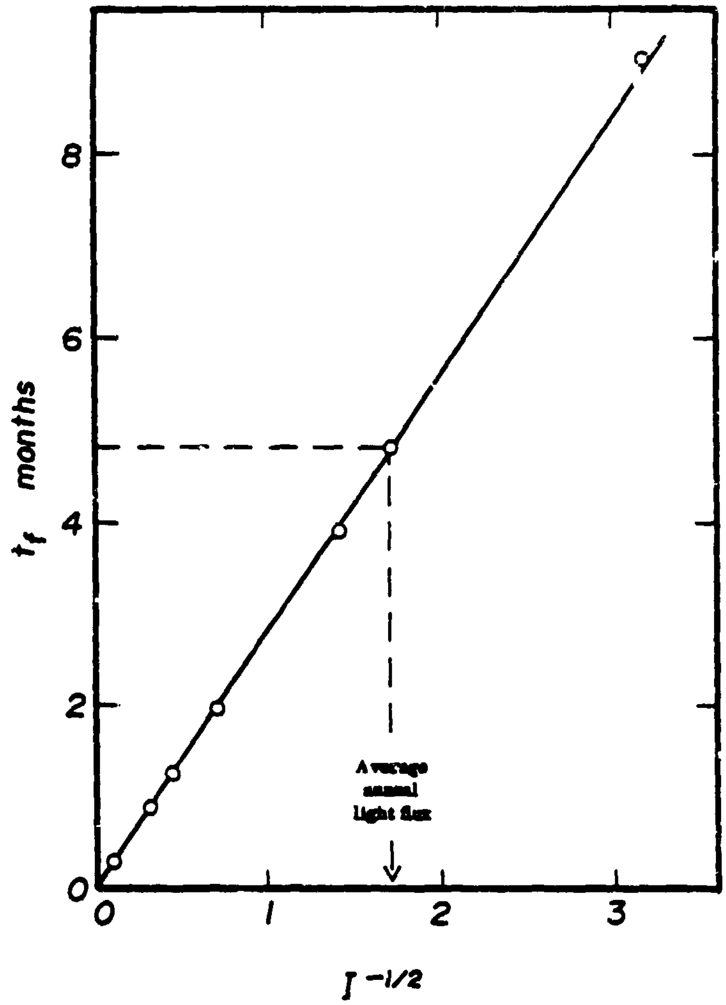


Photooxidation of Unstabilized Polyethylene

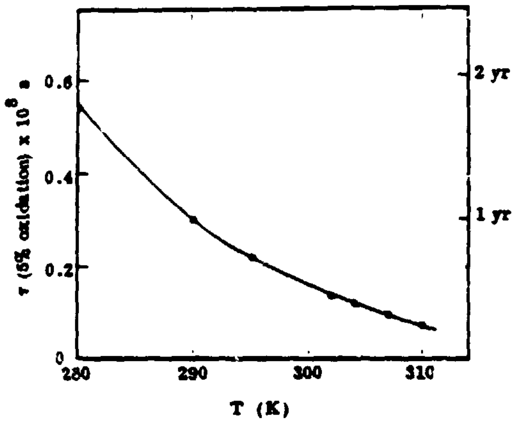
Time to failure as a function of light intensity

$$ROOH \xrightarrow{h\nu} RO\cdot + OH\cdot$$

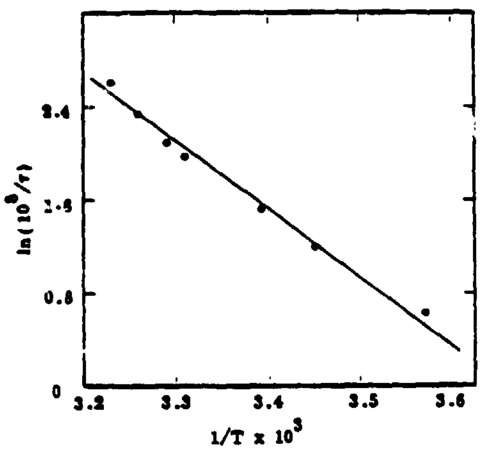
$$Ketone \xrightarrow{h\nu} R\cdot + RC{=}O$$



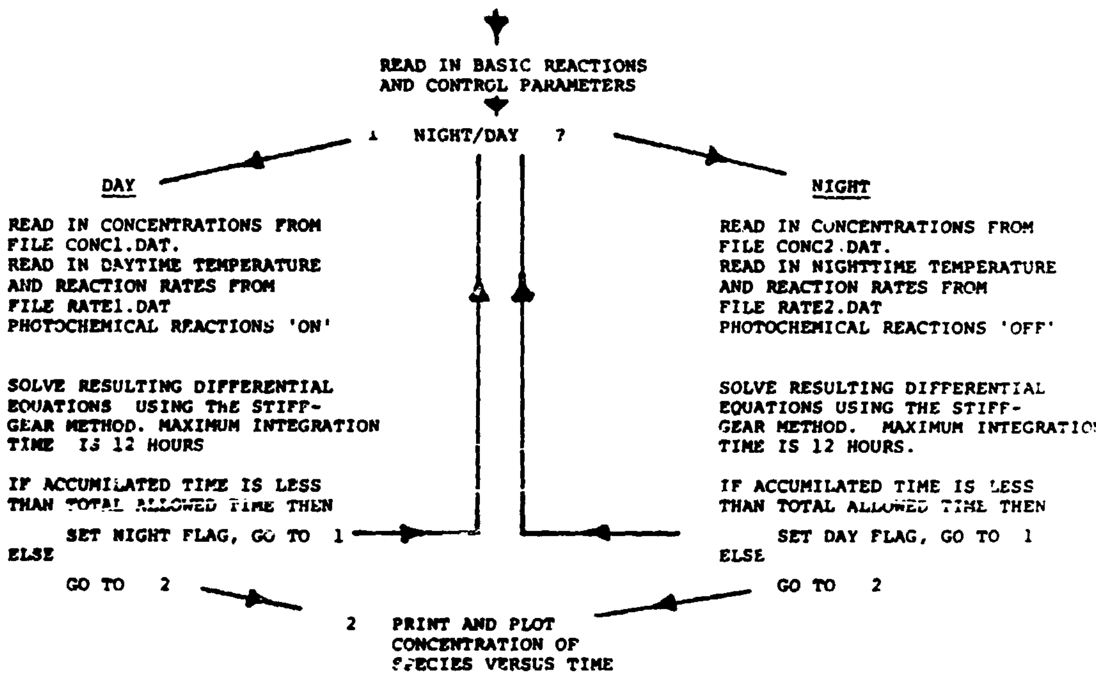
Time to Failure as a Function of Temperature



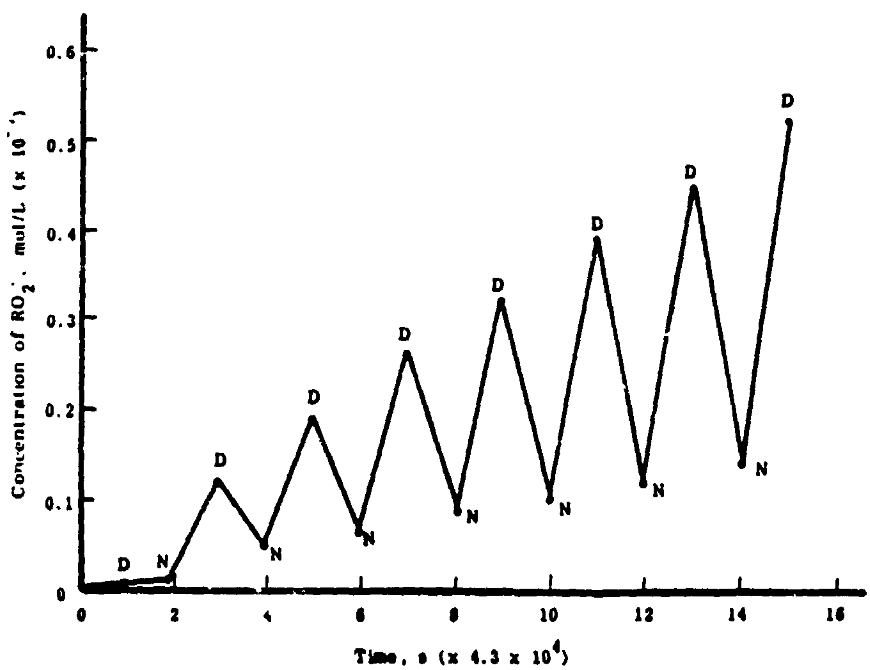
Arrhenius Plot of Rate of Oxidation (k Versus 1/T)



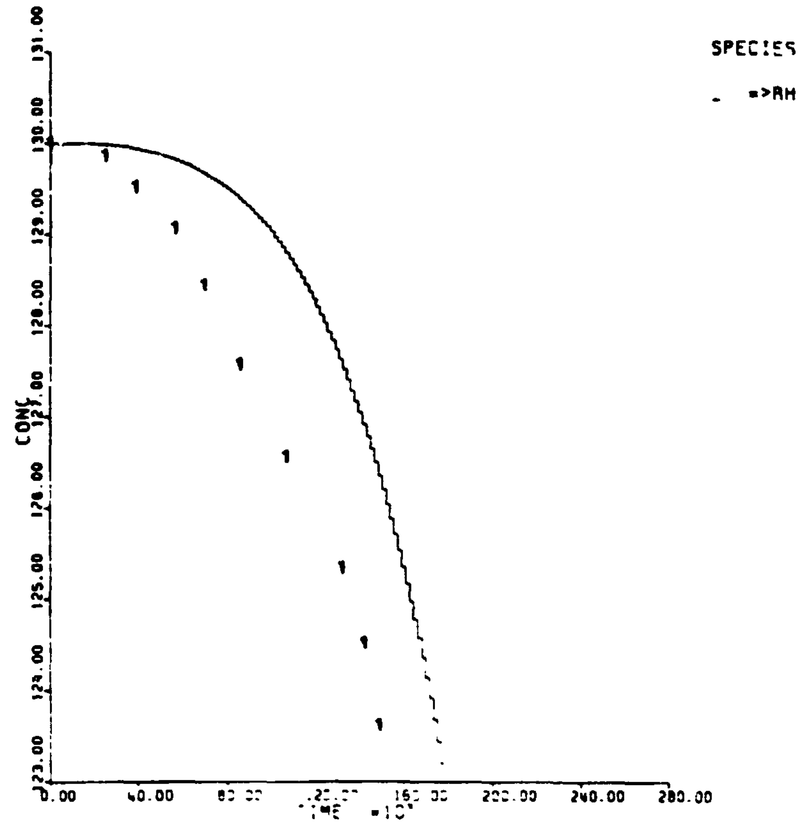
Flow Diagram for Computer Modelling



Concentration of $RO_2\cdot$ Versus Time



Concentration of RH Species Versus Time



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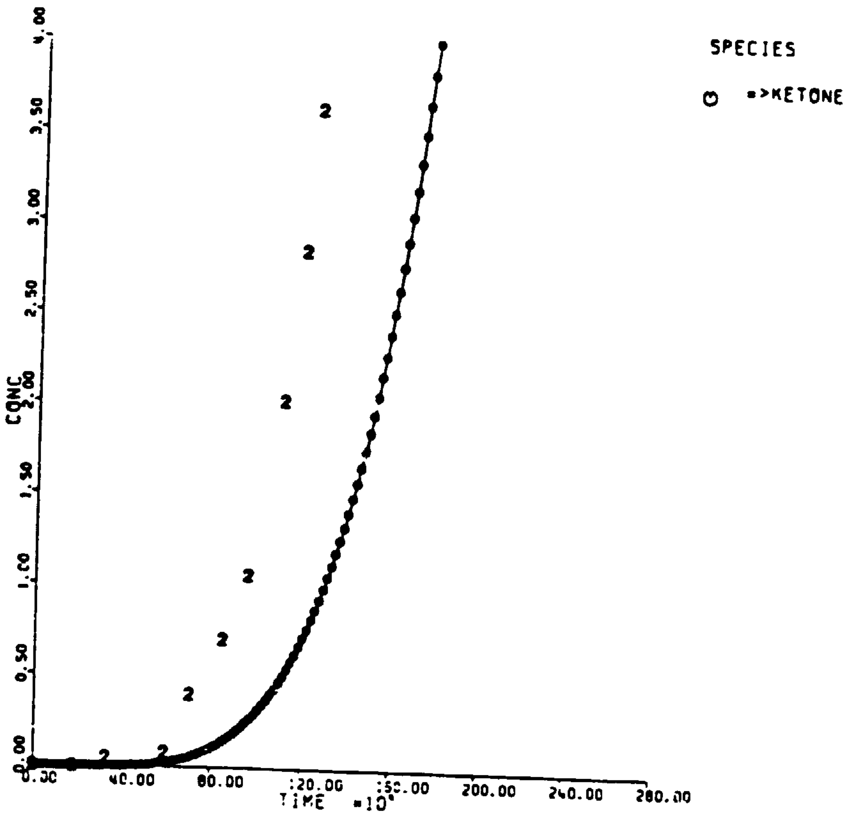
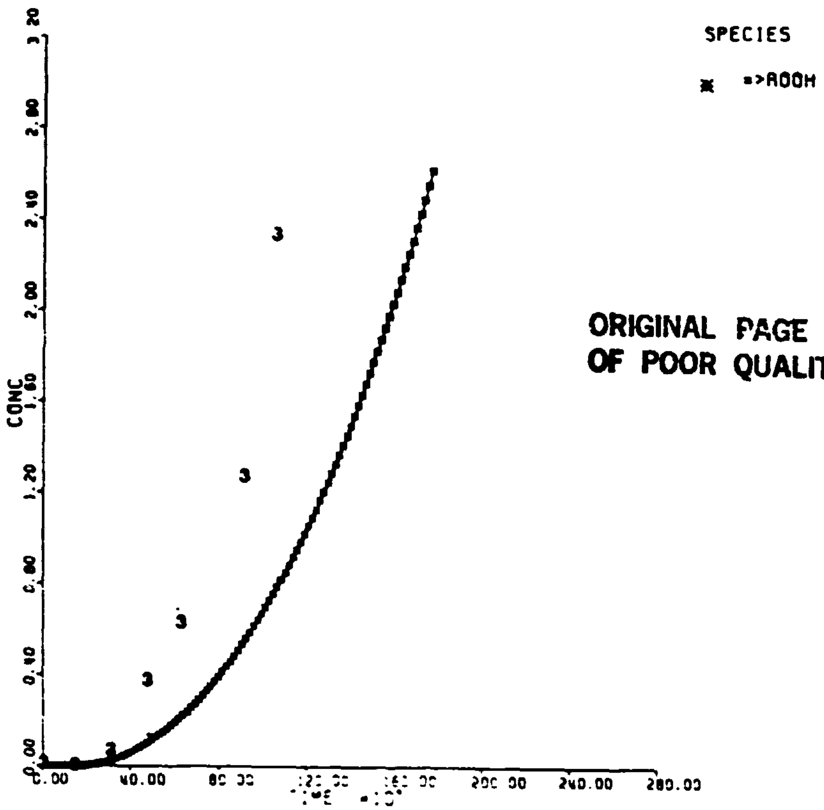
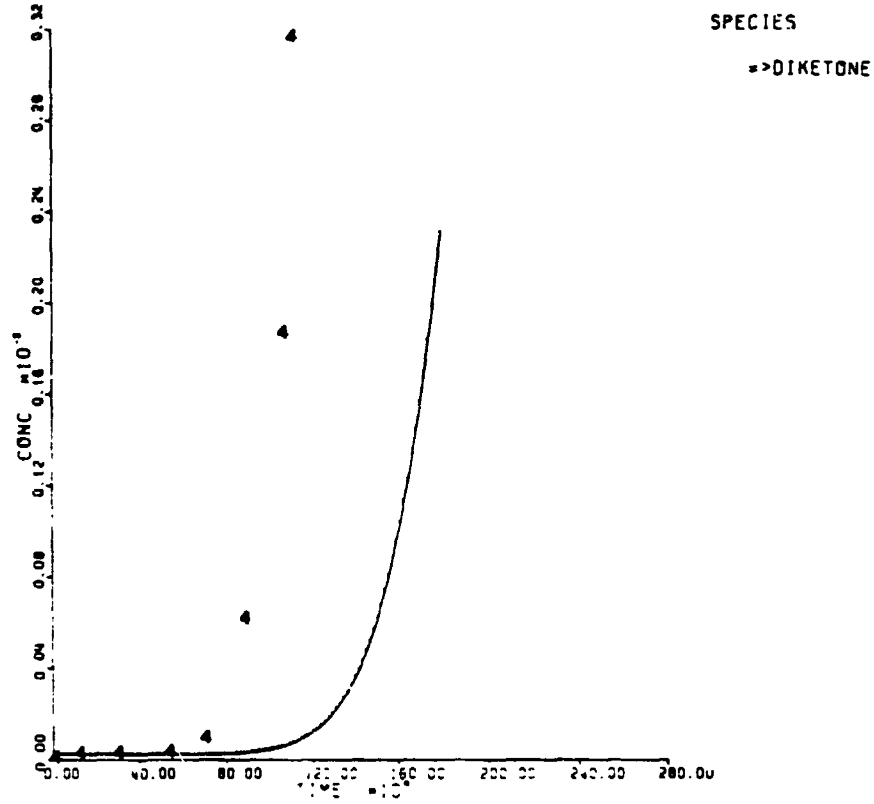
Concentration of Ketone Species Versus Time



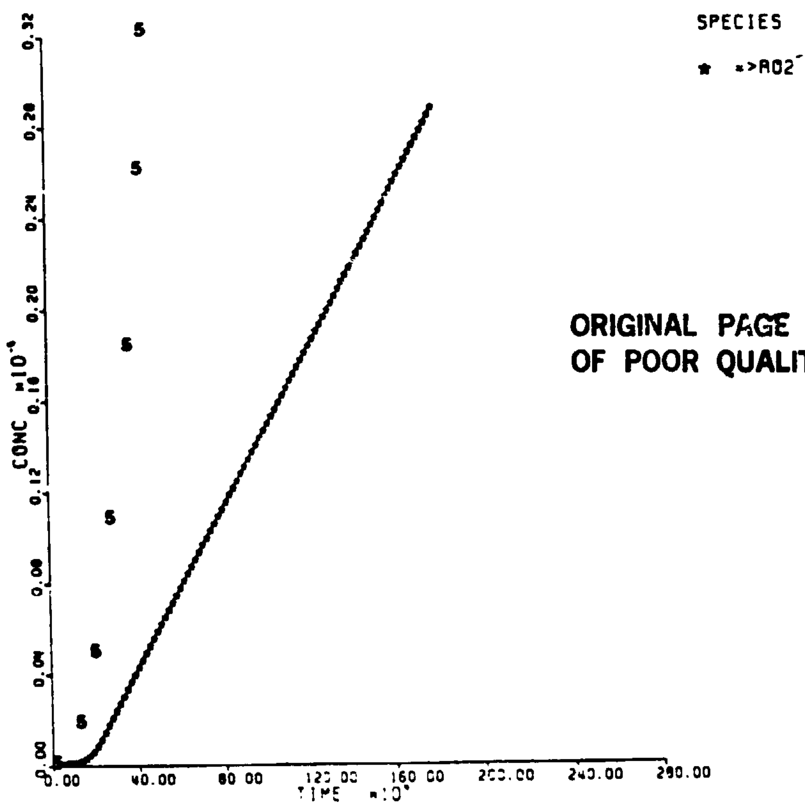
Concentration of ROOH Species Versus Time



Concentration of Diketone Species Versus Time



Concentration of ROO• Species Versus Time



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Concentration of ROO• Species Versus Time