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## Pyrolysis Kinetics of Ethyl Nitrate

Betty Meihorng Lee

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PYROLYSIS KINETICS OF  
ETHYL NITRATE

by

Betty Meihorng Lee

A Thesis  
Submitted to the  
Faculty of the School of Graduate  
Studies in partial fulfillment  
of the  
Degree of Master of Arts

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Kalamazoo, Michigan  
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## TABLE OF CONTENTS

	PAGE
INTRODUCTION . . . . .	1
Background . . . . .	2
Kinetics in a Flow System . . . . .	6
EXPERIMENTAL . . . . .	10
Apparatus and Procedure . . . . .	10
Material . . . . .	14
Analytical Techniques . . . . .	15
Sample Calculation . . . . .	16
RESULTS AND DISCUSSION . . . . .	18
Reaction Products . . . . .	18
Kinetic Results . . . . .	18
Reaction Mechanism . . . . .	25
SUMMARY . . . . .	31
APPENDICES . . . . .	32
Appendix A. Kinetic Data . . . . .	33
Appendix B. Calibration Data . . . . .	35
Appendix C. Analysis of Uncertainties . . . . .	36
BIBLIOGRAPHY . . . . .	41

# LIST OF FIGURES

FIGURE		PAGE
1.	Flow System . . . . .	11
2.	Percentage decomposition vs. contact time at 515°K . . . . .	19
3.	Percentage decomposition vs. contact time at 523°K . . . . .	20
4.	One half order plot of rate data at 515°K .	21
5.	One half order plot of rate data at 523°K .	22
6.	One half order plot of rate data at 533°K .	23
7.	Arrhenius Plot . . . . .	26

## INTRODUCTION

Detonation is the result of rapid exothermic chemical reactions, initiated by external stimuli (shock waves, heat, radiation, etc.). Understanding of this important process requires assessment of the role that these chemical reactions play and the correlation of chemical properties with detonation sensitivity by the determination of the rates and mechanisms of the chemical reactions involved. The objective of this research is to study the pyrolysis rate and mechanism of a detonation sensitive compound because it is believed that pyrolysis is one of the most important steps in the detonation process. The eventual goal of studies, directed at a better understanding of the process of detonation, is the alteration of the detonability of a particular substance by one of the following: modification of chemical properties by a minor alteration to the basic substance molecule and/or introduction of environmental changes (additives, stabilizers, etc.) which will modify the reactions involved.

In the selection of the reactant to be studied, consideration was given to the complexity of the system so that the results could be satisfactorily interpreted. Thus, the pyrolysis rates and mechanisms of ethyl nitrate were studied since this compound is used as a detonation

sensitivity standard and has relatively few atoms per molecule for this type of reactant, resulting in the number of products from its pyrolysis being minimal. Although kinetic studies of the pyrolysis of ethyl nitrate at low temperature have been reported,<sup>1,2,3</sup> the very rapid reactions involved in detonation necessitate the use of higher temperatures than those previously employed, which may result in significant changes in the pyrolysis mechanism.

### Background

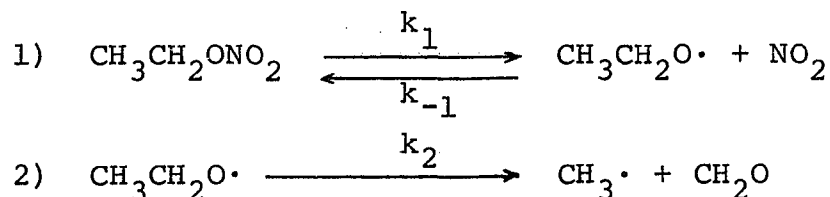
At present there is no universally acceptable mechanism to explain the initiation of detonation. A possible qualitative description of the detonation process can be given as follows: The sample is subjected to a thermal or mechanical shock (pressure pulse). In the latter case the shock is transformed into heat (compression, internal friction, etc.) which causes pyrolysis to take place, principally in the vapor phase. If the reaction rate is above a minimum value and accompanied by a large evolution of heat, the reaction can reinforce the original shock and provide additional energy which can be transferred to the condensed phase. The reactions involved, gas phase and surface, can propagate and accelerate through two different mechanisms, thermal and branch chains. Considering the reaction times and temperatures involved it is unlikely

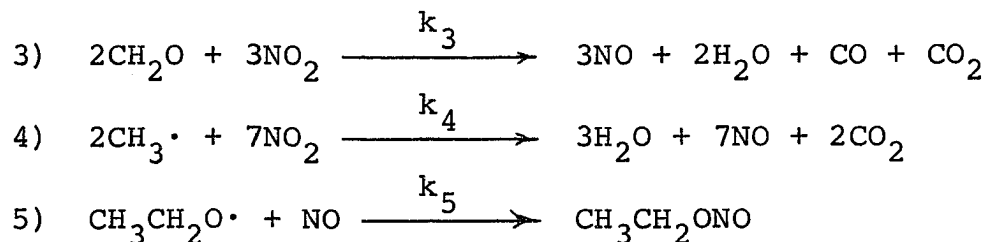


that the reactions can take place in the bulk condensed phase without vaporization occurring first; however, surface attack by radicals may contribute to the overall process.

It is important to note at this point that acceleration of the reaction does not depend directly on the rate of disappearance of the reactant; this step is endothermic due to bond breakage. On the other hand, the reaction acceleration does directly depend on the steps leading to the evolution of heat and/or the branching steps in the formation of radicals. Therefore, it would be possible to influence a substance's detonation sensitivity without changing its rate of disappearance by altering the later steps in its pyrolysis mechanism.

Levy<sup>1,2</sup> studied the kinetics of the thermal, vapor phase decomposition of ethyl nitrate in the temperature range of 161° to 201°C with reaction times of 10 to 150 minutes, using a static system. The concentrations of products and unused reactant were followed directly by infrared spectroscopy. The major product was ethyl nitrite, some methyl nitrite and methyl nitrate were found also. The following mechanism was postulated:





The rate expression after applying the steady-state treatment to steps 1 and 5 was found to be

$$\frac{-d(\text{CH}_3\text{CH}_2\text{ONO}_2)}{dt} = \frac{k_1(\text{CH}_3\text{CH}_2\text{ONO}_2)}{1 + k_{-1}(\text{NO}_2)/k_5(\text{NO})}$$

Step 2 was not considered in the steady-state treatment because ethyl nitrite was the major product, thus the contribution of the decomposition of the ethoxy radical is relatively minor at low temperatures. The expression predicts that with the addition of nitric oxide the rate should approach a limiting value corresponding to  $k_1$ . This limit is reached when step 5 has been so accelerated that the reverse of step 1 is negligible. The expression for the rate constant obtained over the temperature range of 161° to 181°C was

$$k = 10^{16.8} \exp(-41,200 \pm 500) / RT \text{ (sec}^{-1}\text{)}$$

This expression was determined under conditions which suppressed the reverse reaction in step one, thus, could be equated to  $k_1$ . It should be noted that steps 3 and 4 are simply attempts to explain the evolution of the final

products and kinetically have no significance since they are condensations of many steps and do not contribute to the disappearance of reactant.

Pollard and Marshall<sup>3</sup> studied the kinetics of the thermal decomposition of ethyl nitrate in the temperature range 175° to 205°C; reaction rates were measured using a pressure-rise static system. The reaction times were 5 to 25 minutes. The rate constant for the initial first order rate was expressed by the following equation

$$k = 10^{14.7} \exp(-38,000 \pm 380) / RT \text{ (sec}^{-1}\text{)}$$

Final products were CO, CO<sub>2</sub>, NO, N<sub>2</sub>O, N<sub>2</sub> and a possible trace of H<sub>2</sub>, as well as ethyl nitrite and NO<sub>2</sub>. Both NO and NO<sub>2</sub> retarded the rate of reaction as measured by the rate of change in total pressure. A cursory examination of the reaction was made at 300°C using a flow system. At this temperature, additional products were found to be formaldehyde, methane and ethane. Thus the mechanism step



was presumed to be more important as the temperature increased.

It should be noted that there appears to be an apparent disagreement between the two sets of results first discussed, i.e., the rate is increased by NO addition in the first case<sup>1,2</sup> and decreased in the second.<sup>3</sup>

However, this may be resolved by considering that in the later study, Pollard and Marshall followed the rate by the time rate of change of the total pressure, whereas Levy observed the concentration of reactant directly. Thus, the rate of pressure rise may have decreased, while the reactant was actually consumed at a faster rate, due to side reactions. This problem points out the necessity of direct observation of the reactant rather than the observation of some composite property in kinetic studies.

The present investigation of the pyrolysis was performed in a flow system in the temperature range of 242° to 260°C, at about one atmosphere total pressure and with contact times (reaction times) of 1 to 11 seconds. The initial mole percents of reactant in the carrier gas ranged from 0.5 to 2.0. Although the temperatures are still not high enough to be comparable to those initiating detonation, the results of this study are considerably different from those previously reported.

#### Kinetics in a Flow System

The kinetic equations applicable to plug-flow and stirred-flow reactors are presented in the following paragraphs; the main advantage of the latter will become apparent from the discussion.<sup>4</sup>

If a mixture of gases is passed through a tubular reactor of a constant cross-sectional area and there is no longitudinal mixing (plug-flow) within the reactor, the change in the number of moles of component  $i$  with time in a volume unit ( $dV$ ) is given by

$$dn_i/dt = r_i dV - udc_i \quad (1)$$

$dV$  = cylindrical volume element

$r_i$  = rate of chemical reaction; it is a function of the rate constants of all reactions involving component  $i$  and of the various concentrations in the volume element.

$u$  = volume rate of flow of the reaction mixture

$c_i$  = concentration of component  $i$

At steady state, Eq. 1 becomes

$$r_i dV = udc_i$$

or

$$r_i = (u/dV) dc_i \quad (2)$$

If, for a constant flow system,  $dV/u$  is replaced by  $dt$ , the resemblance between Eq. 2 and the familiar equations for the closed-system kinetics becomes obvious

$$r_i = dc_i/dt \quad (3)$$

If, instead of the tubular reactor, a stirred-flow reactor is used, the concentrations of the reactants and the

products are considered uniform throughout the reactor and equal to the exit concentrations. Therefore, in Eq. 2 the volume element  $dV$  may be replaced by  $V$  (the total reactor volume), and  $dc_i$  may be replaced by  $(c - c_0)$ . Thus, Eq. 4 is obtained

$$r = u (c - c_0) / V \quad (4)$$

$c_0$  = initial concentration of component

Equation 4 applies to any component of the system. Again, if the flow rates are assumed constant, Eq. 4 can be rewritten

$$r = (c - c_0) / t \quad (5)$$

$t$  = residence or contact time =  $V/u$

Equation 5 enables an explicit determination of the rate of reaction. By changing the initial concentrations and/or flow rates, the form of the rate equation and the rate constants can be determined without requiring integration.

The above equations apply to any order reaction, simple or complex. For example, consider the simple first-order reaction



where

$$r = \text{rate} = -kc \quad (6)$$

combining equation 3 and 6 and integrating, the result for

a tubular plug-flow reactor is:

$$k = 1/t \ln (c_0/c) \quad (7)$$

$c$  = concentration of A at time  $t$

$c_0$  = initial concentration of A

On the other hand, for a stirred reactor, the equalities in equations 5 and 6 give:

$$r = (c - c_0)/t = -kc$$

or

$$k = (c_0 - c)/ct \quad (8)$$

In the case of the stirred reactor, integration is unnecessary to evaluate the rate constant. This is particularly useful when dealing with reactions which have a complex rate expression since direct plots of rate versus concentration can be made, which allows a more rapid and accurate interpretation of the kinetic data. Kinetic data obtained from stirred-flow reactors are called differential rate data since the differential rate is explicitly determined.

## EXPERIMENTAL

### Apparatus and Procedure

The flow system used in the present kinetic study is schematically presented in Figure 1. Helium, used as the carrier gas, was purified by passing through activated charcoal at liquid nitrogen temperature. The helium flow was controlled by a conventional pressure regulator and needle valve, and measured by a capillary flowmeter, F (di-n-butyl phthalate was used as the manometric fluid). The flowmeter was calibrated in terms of pressure drop versus millimole per minute flow rate using a "Precision" wet testmeter.

The carrier gas was heated, prior to the point of injection of ethyl nitrate, by passage through the preheating channel, P. A coil of chromel A, 22 B & S gauge wire wrapped around the pyrex tube and insulated by asbestos served as the heating element. Ethyl nitrate injected at point S was vaporized and carried to the mixing chamber, M, by the carrier gas. The injection system consisted of a motor driven, 2 ml tuberculin syringe, Sage syringe pump, and a hypodermic needle silver soldered into a metal ball joint which connected the needle and syringe to the glass flow system. The injection rates were calibrated by the injection of mercury into weighed vials. A three-way



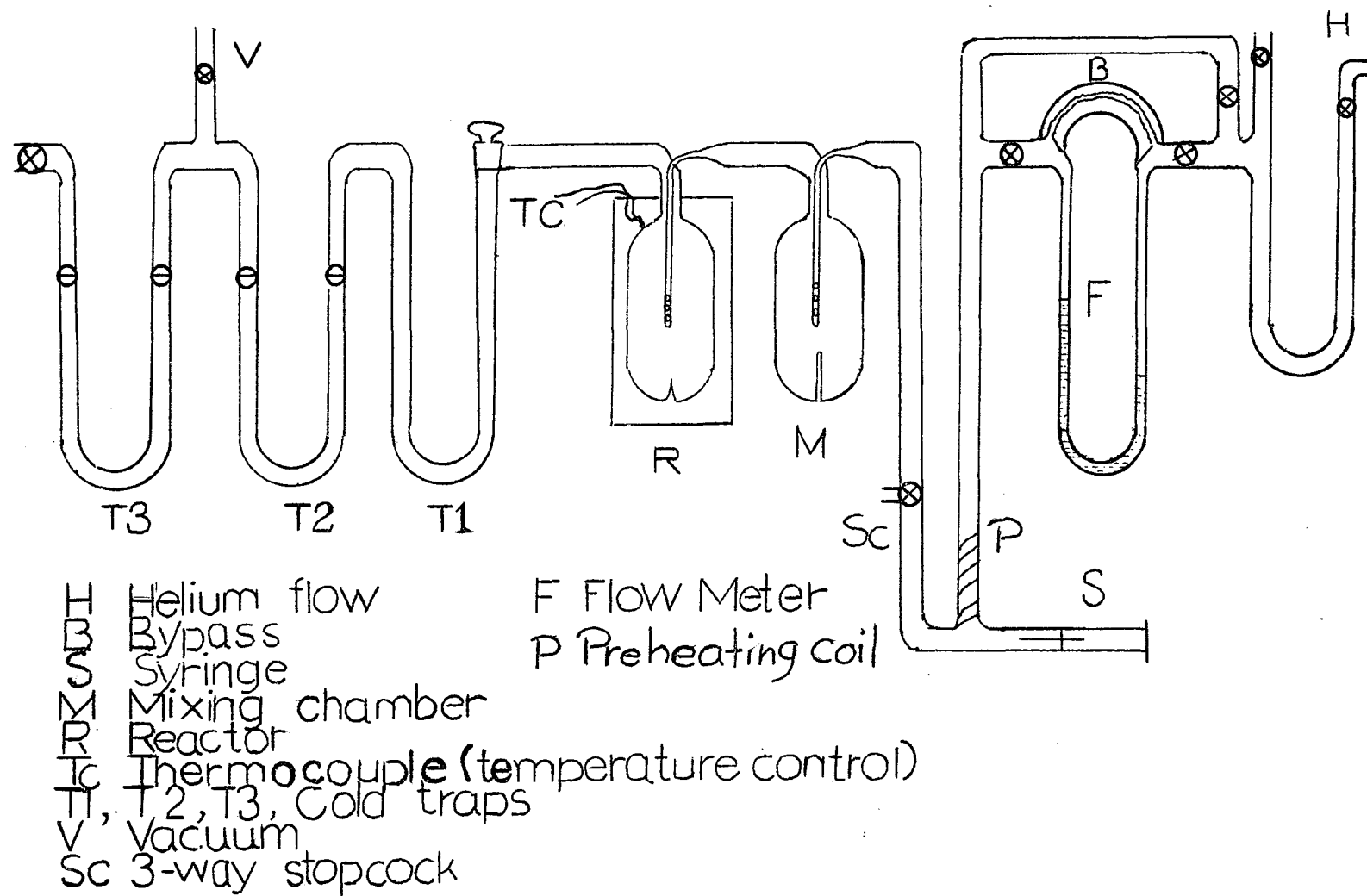


Fig.1. Flow System.

stopcock, Sc, was placed between the injection section and mixing chamber which directed the flow of the stream through the reactor or vented the stream to the room.

The mixing chamber, M, and reactor, R, were pyrex tubes, 40 mm in diameter with a total volume of 80 ml. A 4 mm tube which extends from the bottom to the center of the reactor was used for a thermocouple well for temperature measurement. The gas inlet is a 4 mm tube with several holes at the end to act as jets for stirring, and extended from the top of the reactor to its center. The outlet was concentric with the inlet tube. This reactor design provides efficient stirring as shown in previous studies.<sup>5</sup>

The reactor is enclosed in a wire wound tubular furnace. The furnace consisted of a stainless steel liner, with two concentric windings (about 8 ohms each of 22 B & S gauge chromel A wire) extending its full length. Asbestos was used as the insulating material. The outer winding was powered through a variac which was connected directly to the main power line; the inner winding was powered through the temperature controller. A Honeywell Versatronik controller, model R7161 H, was used to regulate the temperature. A chromel-alumel thermocouple placed between the reactor and furnace walls, was used as the controller sensor. Two additional chromel-alumel thermocouples located in the thermocouple well were used to measure the temperature.

The trapping section consisted of three "U" traps; traps 2 and 3 were packed with glass beads to increase the cold surface area. Liquid nitrogen was the coolant for these three traps.

The procedure for a typical experiment after the proper reactor temperature was attained, was as follows: First, from the desired contact time and the volume of the reactor, the total flow rate can be calculated. Based on this flow rate, the pressure drop in the flowmeter can be found from the flowmeter calibration curve. From the specified mole fraction of ethyl nitrate in the gas stream and the total rate of flow, the injection rate of the syringe can be calculated; the setting on the syringe pump is obtained from the syringe calibration curve. The helium flow rate was set at the proper value while the stream is vented to the room through the three-way stopcock, and the injection system was turned on. The outlet of the syringe was carefully watched to avoid injection of the liquid reactant into the gas stream, which would lead to poorly defined concentrations. The helium stream was maintained hot enough to vaporize the reactant without decomposing it. The partial pressure of ethyl nitrate was maintained below its vapor pressure at room temperature. The injection was left on long enough to observe the reactant vaporizing smoothly into the stream

before it was turned off and helium flow was continued for two minutes to flush the system. Following this, the helium stream was directed to the reactor and traps by turning the three-way stopcock. At this time, the "U" traps are cooled with liquid nitrogen. The injection system is turned on again and the input of ethyl nitrate is timed so that the total quantity of reactant injected will be known. At the end of a preset time interval, the injection was turned off and the system was flushed by helium. Then, the helium flow was stopped and the flow system was connected to the vacuum in order to transfer the volatile product and unreacted ethyl nitrate to the traps containing the tert-butyl benzene.

The range of contact time and concentrations were mainly limited to those selected so that the rate of injection of reactant was not too high. A high rate of injection may result in an incomplete vaporization and uncertain concentrations. An increase in the rate of vaporization by excessive heating could cause premature decomposition.

#### Material

Ethyl nitrate, Eastman white label grade, was used without further purification. The measured refractive index was 1.3832 at 22°C; the literature<sup>6</sup> value is 1.3849 at 22°C. A subsequent mass spectrometric analysis was

made of the ethyl nitrate used. It was found from the size of the ion peaks not accounted for by the ethyl nitrate spectrum, that the total impurities would be less than one percent.

Tert-butyl benzene, used as the internal standard for the gas chromatography measurements, was obtained from students' preparations. The middle fraction of the distillate, which boiled at 164-5°C, was used.

#### Analytical Techniques

The volatile products and reactant collected in the traps were transferred under vacuum into the container holding a known weight of tert-butyl benzene for subsequent analysis with an F and M, model 760, gas chromatograph. The nonvolatile residue in the traps was a white solid. The infrared spectrum of this material in a nujol mull was obtained by use of a Beckmann IR-8 spectrophotometer.

Diethylene glycol succinate was the liquid phase on the column in the gas chromatograph used to quantitatively determine the unreacted ethyl nitrate. A calibration curve was constructed by plotting several known weight ratios of ethyl nitrate to tert-butyl benzene against the area ratio obtained from the chromatographic peaks using a 2 micro-liter sample. The selection of tert-butyl benzene as an internal standard was based on its long retention time which

provided a good separation of peaks without overlap of those from the reactant and products. The volatile products of the pyrolysis all had shorter retention times than did the reactant. From the measured area ratio of ethyl nitrate to tert-butyl benzene, one can find the weight ratio. Then, from the known weight of tert-butyl benzene in the container, the amount of unreacted ethyl nitrate can be calculated.

#### Sample Calculation

The definition of the rate of a chemical reaction of the  $n$  th order is:

$$\text{rate} = -dc/dt = kc^n$$

For a stirred flow reactor,

$$\text{rate} = x/t = k(c_0 - x)^n = k(1 - x/c_0)^n c_0^n$$

where  $x$  = the change in concentration of reactant ( $c_0 - c$ ),

$c$  = concentration of reactant at time,  $t$ ,

$x/c_0$  = the fraction decomposed,

$t$  = the contact time, reactor volume/volume rate of flow

$c_0$  = initial concentration of reactant

For example, 26.2% decomposition was obtained from initial concentration of 0.5 mole % of ethyl nitrate in the gas stream at 242°C, 750 mm Hg total pressure, and a helium

flow rate of 30.2 m mole/min. These data are used to calculate the rate below:

Using the assumption of ideal gas behavior, the molar volume of the gas mixture

$$V = 43 \text{ l/mole} = 43 \text{ ml/m mole at } 242^{\circ}\text{C and } 750 \text{ mm Hg.}$$

$$\begin{aligned} \text{Total volume flow rate} &= 30.2 \times 1/(1 - 0.005) \times 43 \\ &= 1.30 \text{ l/min} = 21.7 \text{ ml/sec} \end{aligned}$$

$$\text{Thus, the contact time} = 80/21.7 = 3.7 \text{ sec}$$

where 80 ml = the volume of the reactor.

$$\begin{aligned} \text{Initial concentration} &= c_0 \\ &= 30.2 \times 1/(1 - 0.005) \times 0.005/1.30 \\ &= 0.117 \text{ m mole/l} \end{aligned}$$

$$\begin{aligned} \text{rate} = x/t &= 0.117 \times 0.262/3.68 = k [0.117 \times (1-0.262)]^n \\ &= k (0.0865)^n = 8.3 \times 10^{-3} \text{ m mole/l sec} \end{aligned}$$

The order of the reaction  $n$ , can be obtained from the slope of the graph of log rate versus log concentration. The best value of the rate constant is obtained from the slope of a graph of rate versus  $c^n$  (it was found that in this reaction,  $n = 1/2$ ).

## RESULTS AND DISCUSSION

### Reaction Products

The presence of NO and NO<sub>2</sub> in the pyrolysis products was indicated by the colors observed in the cold traps; the deep blue at low temperature was from condensed N<sub>2</sub>O<sub>3</sub>, the brown from NO<sub>2</sub>.

In addition to the volatile compounds, a large fraction of white polymeric solid was obtained. This solid coated the walls of the flow system and hence a quantitative measurement was not possible. However, a qualitative examination for composition was made. The polymer was soluble in sodium hydroxide and concentrated sulfuric acid but not in water and common organic solvents, such as benzene, chloroform, acetone, alcohol and dimethylsulfoxide. The infrared spectrum revealed major absorptions only at 1217, 1090 and 930 cm<sup>-1</sup>, the latter two were fairly broad bands. None of these bands correspond to absorption characteristic of the functional groups: C=O, NO, NO<sub>2</sub>, ONO<sub>2</sub>, ONO and C=C. On the basis of solubility and infrared spectra, it was concluded that the polymer may be a polyether formed from the aldehydes and radicals.

### Kinetic Results

The results of the flow experiments are illustrated in Figures 2 through 6; the data is tabulated in Appendix A.



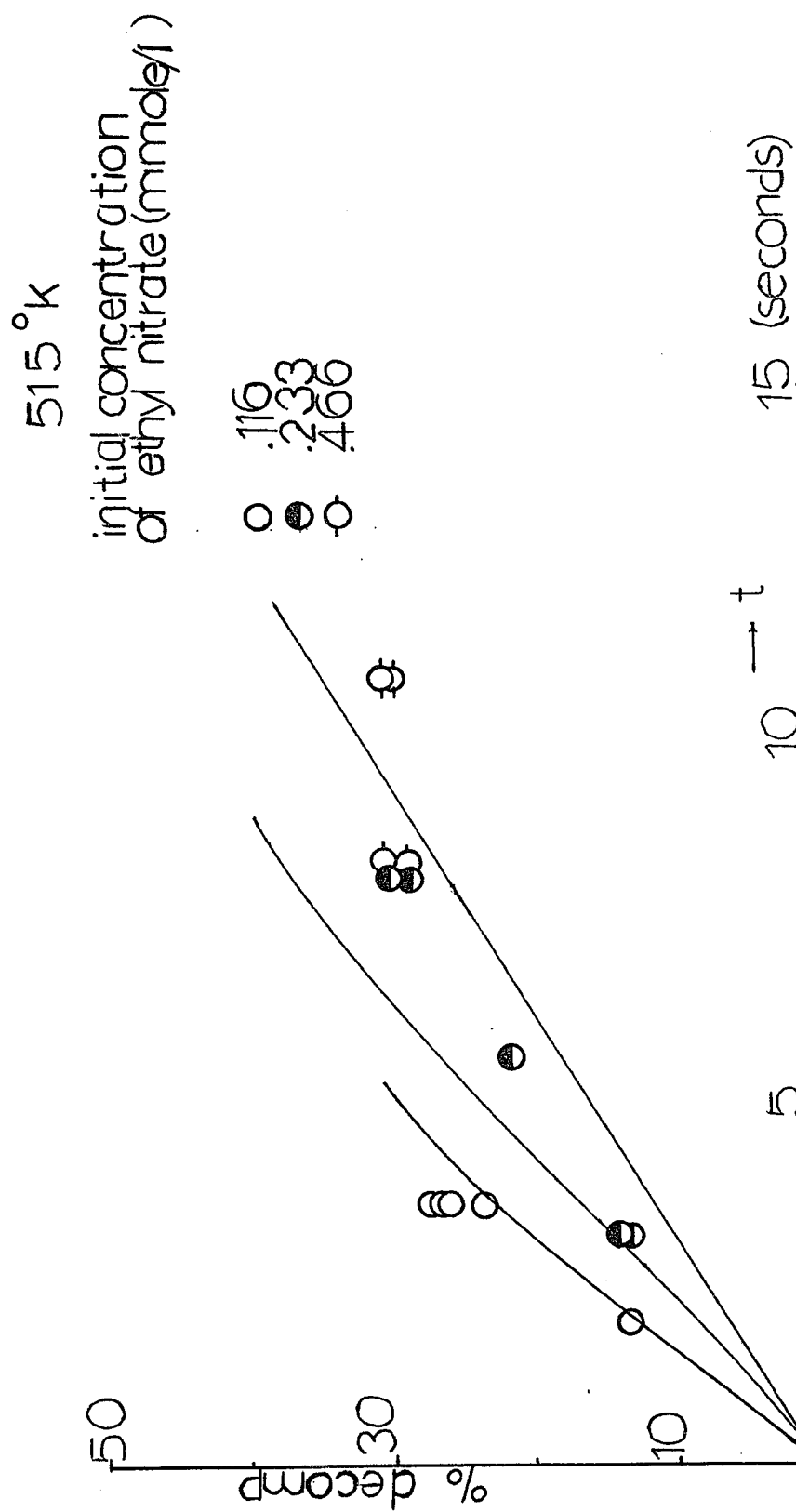


Fig.2. Percentage decomposition vs. contact time.

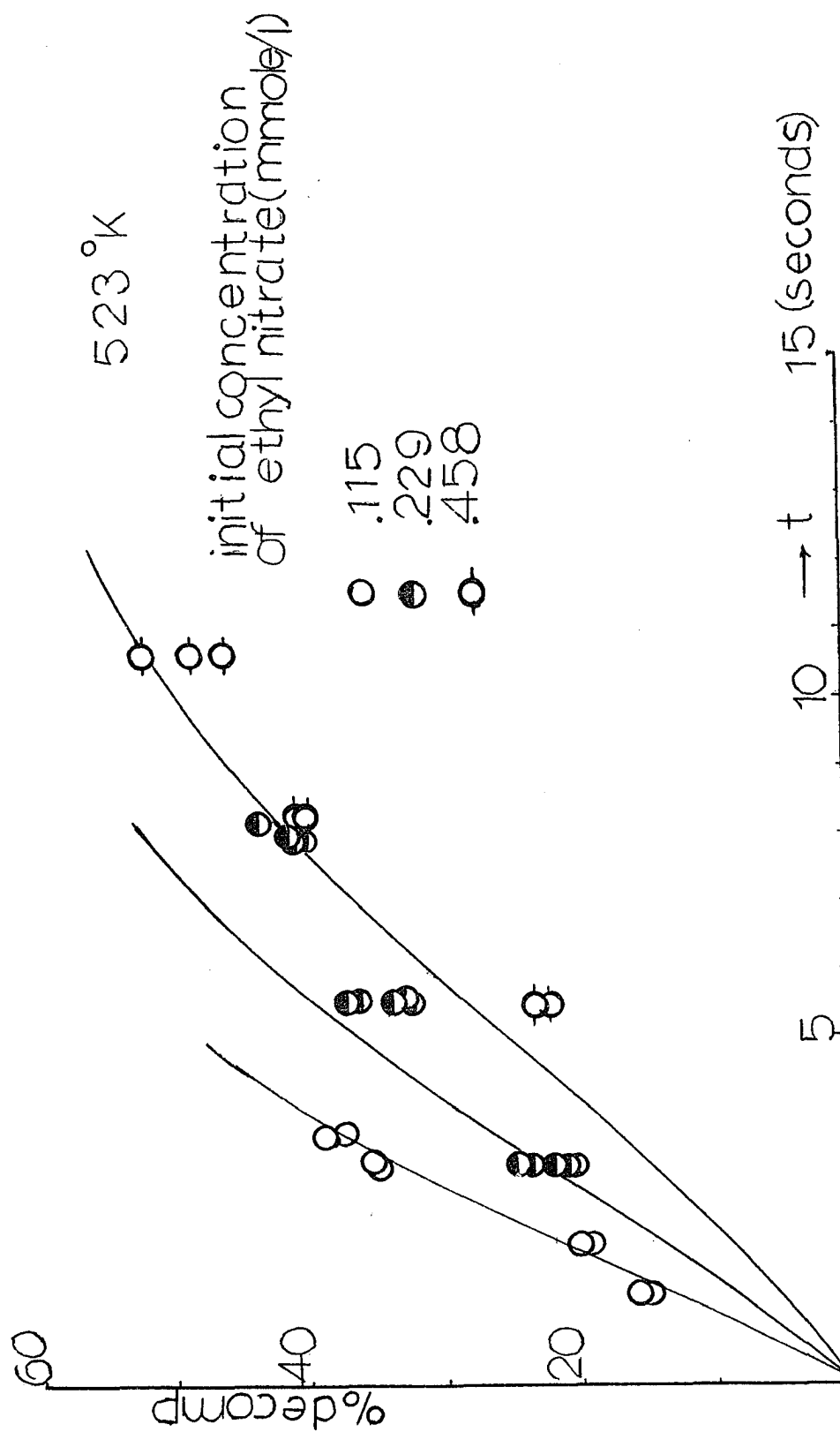


Fig. 3. Percentage decomposition vs. contact time.

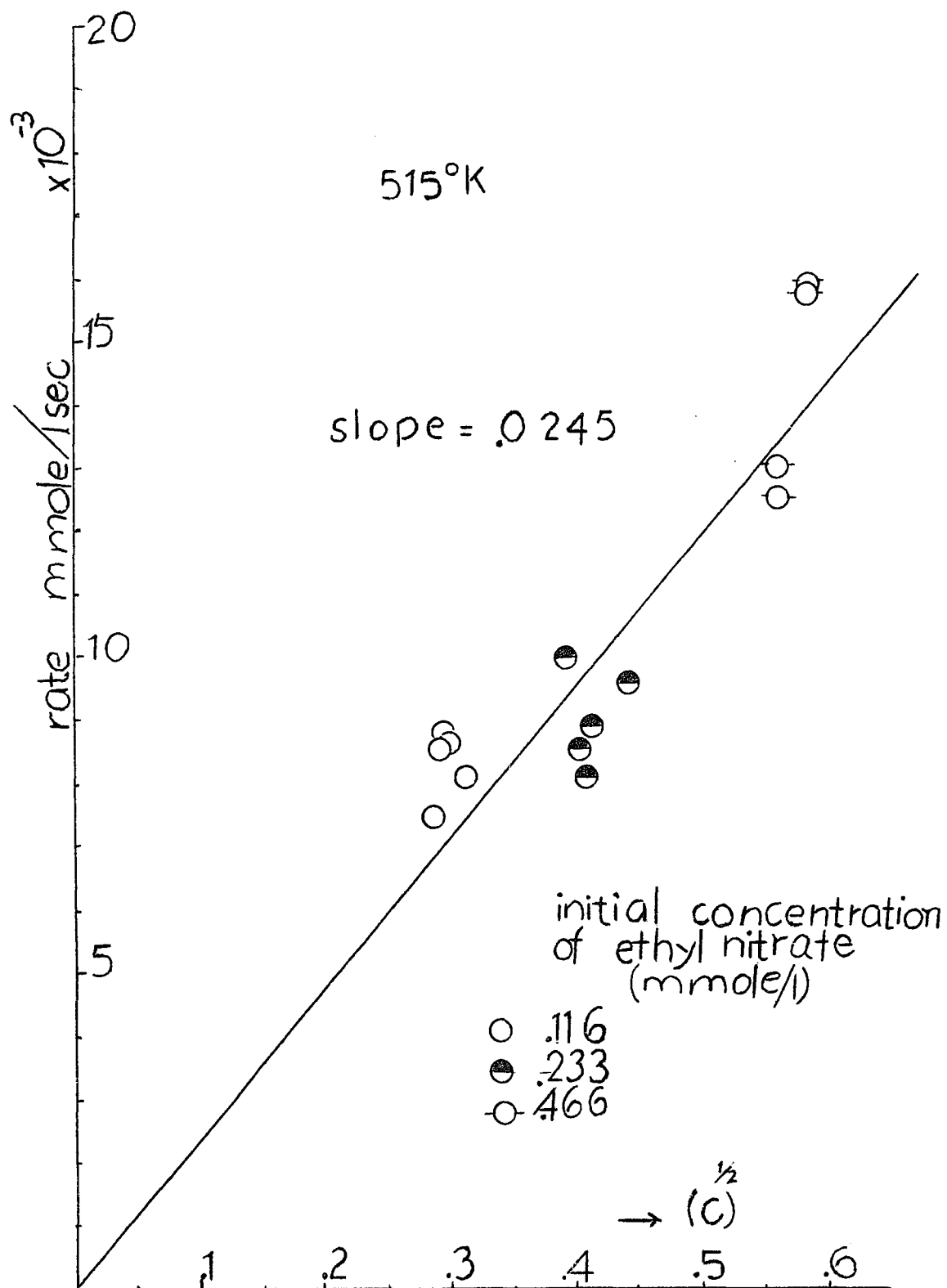


Fig.4. One half order plot of rate data.

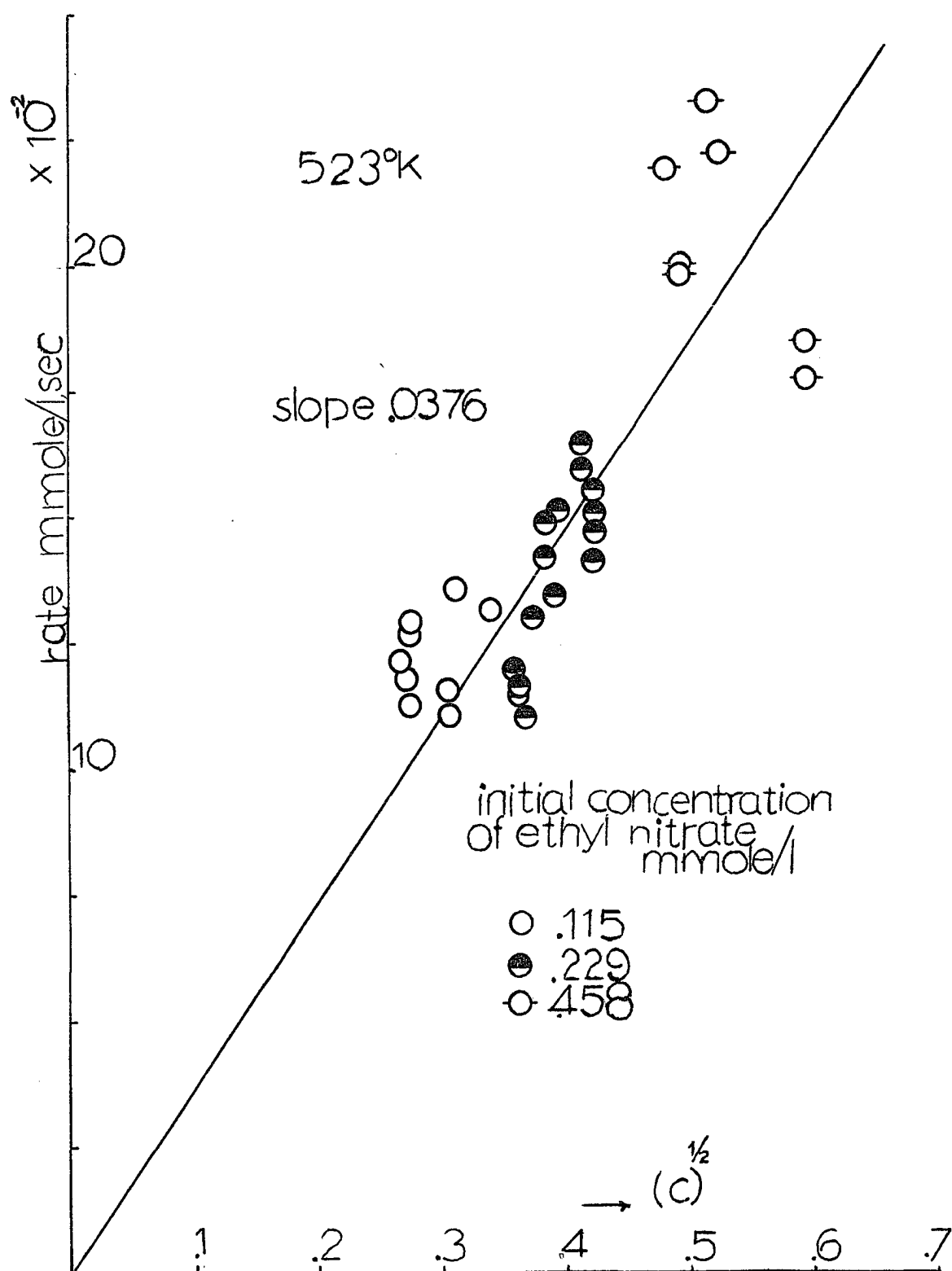


Fig.5. One half order plot of rate data.

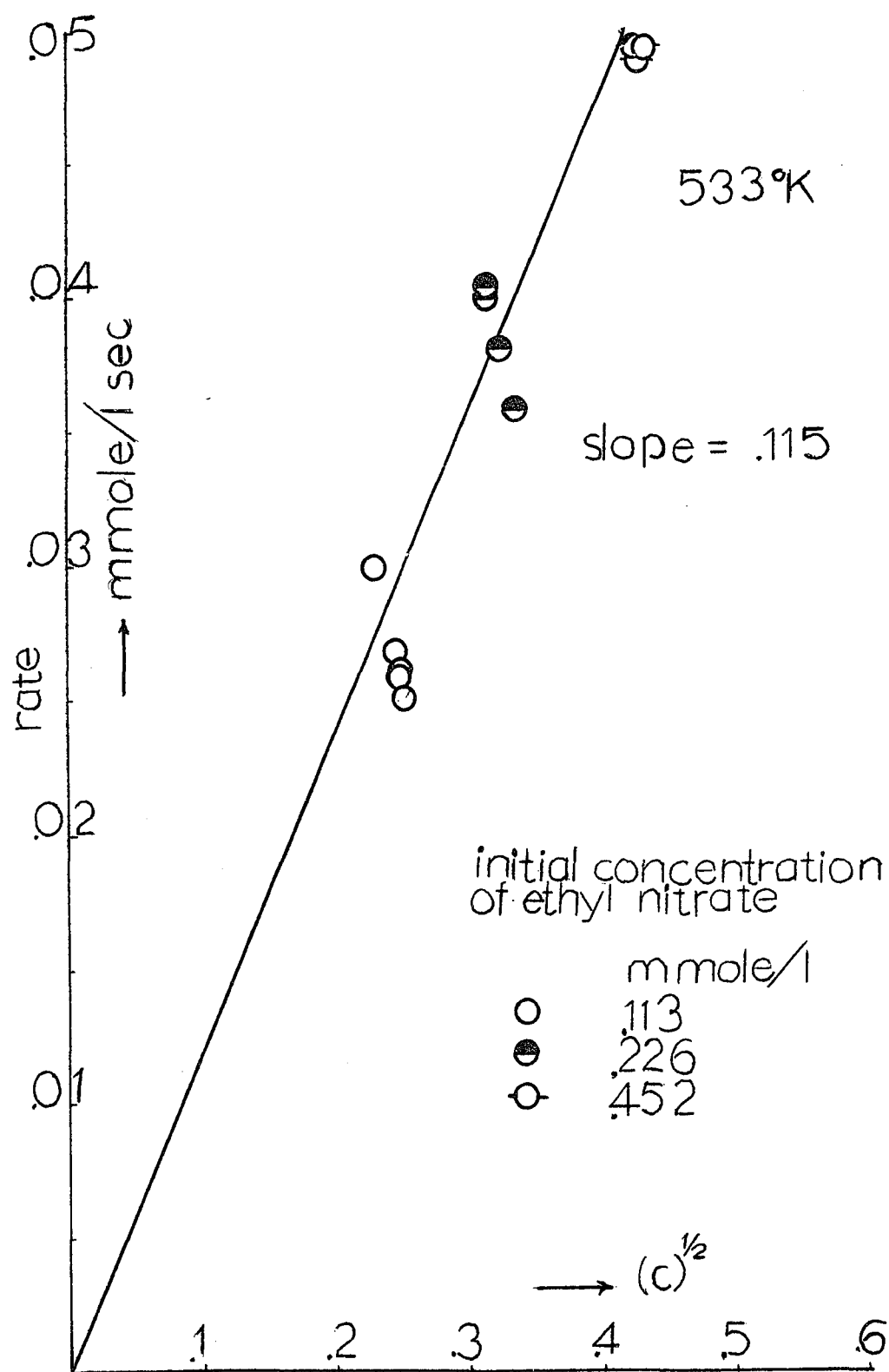


Fig.6. One half order plot of rate data.

Figures 2 and 3 are the percentage decomposition of ethyl nitrate versus contact times at 515°K and 523°K. The curves were obtained from the integrated form of the half order equation (eq. 9) and the rate constants shown in Table 1.

$$(c_0 - c)/c_0 = (kt/2c_0^{1/2}) - (k^2t^2/4c_0) \quad (9)$$

The corresponding graph at 533°K is not shown because only one contact time was used at each concentration. It can readily be seen from Figures 2 and 3, that the percentage decomposition at a given contact time decreases as the initial concentration increases. Thus it can be concluded that the order of pyrolysis must be less than one. With a stirred-flow reactor, a numerical value for the rate is obtained experimentally (as discussed previously):

$$\text{rate} = (c_0 - c)/t = kc^n \quad (10)$$

Thus, the order of reaction,  $n$ , can be obtained from the slope of a  $\log (c_0 - c)/t$  versus  $\log c$  plot. For this reaction the order was found to be about 1/2. The best method for calculating the specific rate constant is from the slope of  $(c_0 - c)/t$  versus  $c^{1/2}$  plot (Figures 4, 5 and 6). The order with respect to concentration is definitely one half, according to the data; however, the scatter and clumping of the points at a particular

initial concentration may indicate a more complex order with respect to time.<sup>7</sup> Additional data would be necessary to clarify this point. The results of these calculations are presented in Table 1. The uncertainties in the individual measurements and their effect on the results is given in Appendix C. An analysis of an Arrhenius plot of the rate constants (Figure 7) yields the following expression for the rate constants:

$$k = 10^{18} \exp(-45,800 \pm 1,200)/RT \text{ mmole}^{1/2} \text{ l}^{-1/2} \text{ sec}^{-1}$$

TABLE 1

## Kinetic Results

T °K	1/T x 10 <sup>3</sup>	$k \times 10^2$ $\text{mmole}^{1/2} \text{l}^{-1/2} \text{sec}^{-1}$	-log k
515	1.942	2.5 ± 0.4	1.612
523	1.912	3.8 ± 0.5	1.425
533	1.876	11.5 ± 1.0	0.939

## Reaction Mechanism

It is apparent that the reaction mechanism under the conditions used in this study is quite different from those previously reported for the pyrolysis of ethyl nitrate at lower temperatures.<sup>1,2,3</sup> This conclusion is based on two observations:

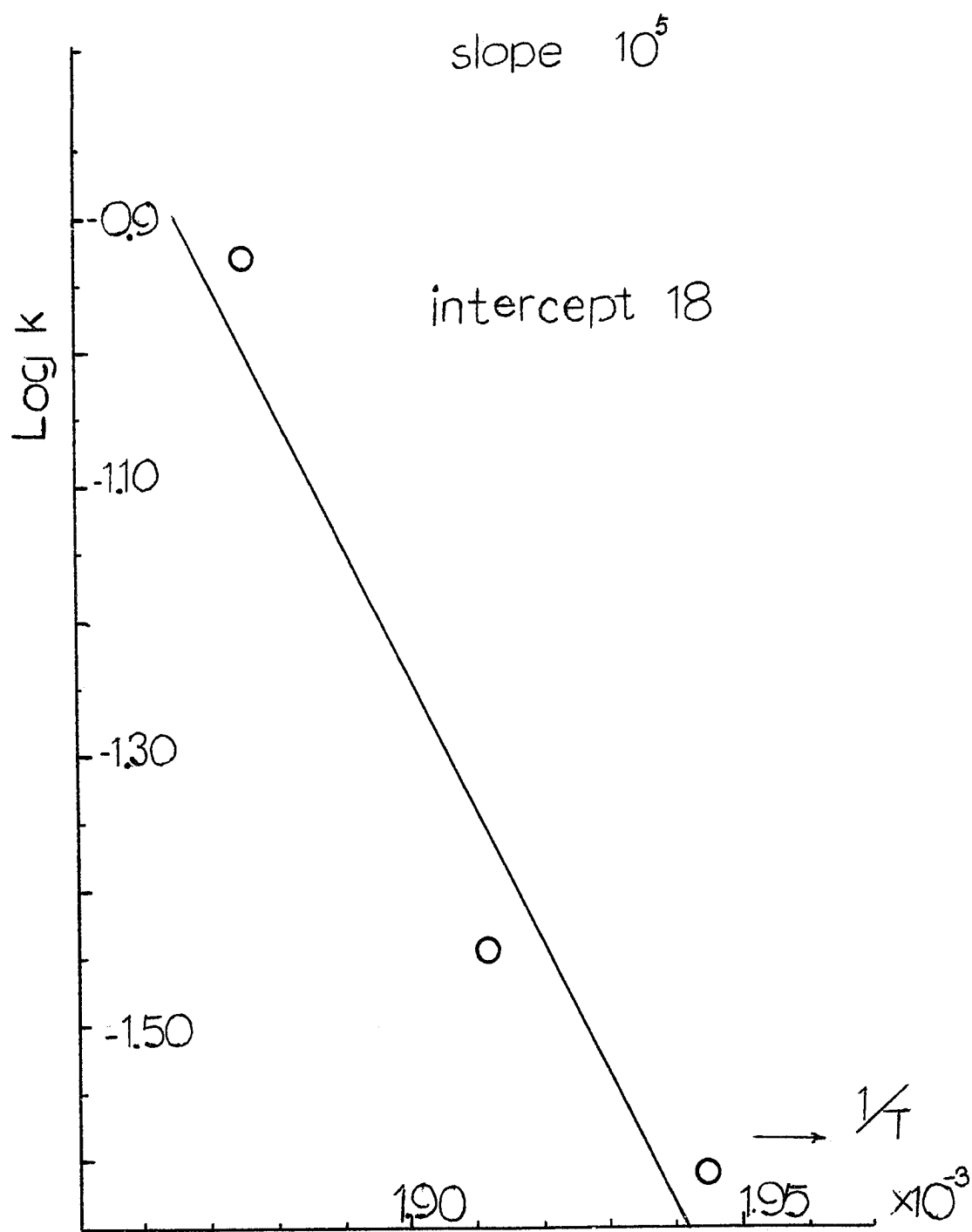


Fig.7. Arrhenius Plot.



- (a) The main organic product previously reported was ethyl nitrite, although some oxidation to CO, CO<sub>2</sub>, etc. took place, whereas an ether type polymer was a major part of the organic product found in this study.
- (b) The reaction kinetics are best represented by a one half order rate expression rather than by one of a first order.

With the large number of atoms and radicals possible in this reaction, in order to interpret the results it is necessary to assume that the oxidative steps in the mechanism, and the subsequently formed radicals, do not significantly influence the rate of reaction. In addition, due to inhibition of the pyrolysis by NO<sub>2</sub> at temperatures up to 200°C, it is apparent that NO<sub>2</sub> does not react directly with ethyl nitrate to promote decomposition.

A satisfactory mechanism must explain:

- (a) the observed rate law for the pyrolysis

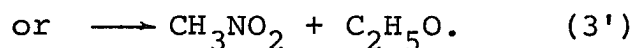
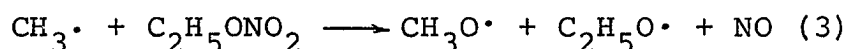
$$\text{rate} = - d(\text{C}_2\text{H}_5\text{ONO}_2)/dt = k(\text{C}_2\text{H}_5\text{ONO}_2)^{1/2}$$

- (b) and the genesis of the observed products.

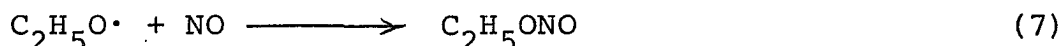
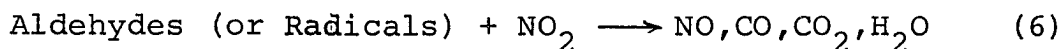
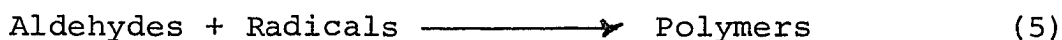
The simplest mechanism that meets these requirements is as follows:\*

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\*Subsequent nuclear magnetic resonance analysis of the polymer and mass spectral analysis of the volatile products have shown that the polymer was probably formed from formaldehyde, and that nitromethane, ethylnitrite and methanol were present in the volatile products and methane was absent. Thus, a hydrogen abstraction step by the methyl radical is excluded from the mechanism.



In addition to the above, there are several steps which lead to product formation but do not enter into the kinetic scheme (polymers are formed in the exit line and traps therefore step 5 does not occur in the reactor):



A steady state treatment of steps 1-4 yields the rate expression

$$-d(\text{C}_2\text{H}_5\text{ONO}_2)/dt = k_2 (k_1/k_4)^{1/2} (\text{C}_2\text{H}_5\text{ONO}_2)^{1/2} \quad (11)$$

In view of the large departure of the current results from those of the previous investigations,<sup>1,2,3</sup> some comparisons and comments are in order. The rate expression by Levy,<sup>1,2</sup> given previously on page 4, contained a denominator which was derived on the basis of the reversal of step one of the mechanism, and the reaction of NO and C<sub>2</sub>H<sub>5</sub>O to form ethyl nitrite. These steps were not

considered as likely possibilities under the current conditions because: (a) at higher temperatures the equilibrium between ethyl nitrate, ethoxy radical and  $\text{NO}_2$  will be well on the side of the products, and (b) the large amount of polymeric product formed, and mass spectral data indicate a relatively minor amount of ethyl nitrite in the products (probably formed as the reaction mixture was quenched after exiting from the reactor). Therefore it is not surprising that the rate equations are considerably different for the high and low temperature reactions.

Although it is apparent that a real shift in the mechanism has occurred, it is worthwhile to discuss certain points concerning the data from the previous studies. Levy measured the rate of disappearance of reactant, but all his measurements were essentially at the same initial concentration of reactant. This can lead to erroneous conclusions since in complex mechanisms involving autocatalysis or inhibition it is possible to have different orders with respect to both time and concentration.<sup>7</sup> In the case of Pollard et al.,<sup>3</sup> the rate of reaction was measured by the change in total pressure, over a range of a factor of two in initial reactant pressure. This also may lead to complications since the pressure of  $\text{NO}_2$  at first increases then decreases at longer times, accompanied by the formation and further reaction of a variety of intermediates

and products, which will obscure the actual behavior of the reactant. It can be concluded that in order to obtain unambiguous kinetic data, the concentration of reactant must be measured as a function of time and a wide range of initial concentration must be used.

## SUMMARY

The pyrolysis rate and mechanism of ethyl nitrate have been studied in the temperature range of 242-260°. The reaction kinetics were found to be one-half order with respect to the reactant; a major portion of the organic product was a polyether, probably formed from aldehydes. The activation energy and frequency factor were determined to be 45.8 kcal/mole and  $10^{18} \text{ (mmole/l.)}^{1/2} \text{ sec}^{-1}$ , respectively. These data are consistent with a radical chain mechanism in which termination occurs through the interaction of two of the monomolecularly decomposing chain-carrying species, which is the ethoxide radical in the proposed mechanism.

## APPENDICES

## Appendix A. Kinetic Data

### Symbols:

$[c_0]$  = initial concentration of ethyl nitrate (m mole/l)

$t$  = contact time (sec)

% = % decomposition

$x$  = concentration of ethyl nitrate reacted

$x/t$  = rate (m mole/l-sec)

$(c)$  = concentration of ethyl nitrate at time  $t$  (m mole/l)

### Data at 515°K (242°C)

$[c_0]$	$t$	%	$x/t$	$(c)$	$(c)^{1/2}$	$-\log \frac{x}{t}$	$-\log (c)$
0.116	2.0	13.5	0.00785	0.100	0.316	2.105	1.000
	3.7	27.3	0.00870	0.0844	0.290	2.066	1.077
		23.5	0.00750	0.0833	0.288	2.300	1.078
		26.2	0.00835	0.0865	0.294	2.091	1.064
		26.5	0.00845	0.0860	0.293	2.076	1.066
0.233	3.2	13.8	0.0100	0.201	0.450	1.996	0.697
		13.0	0.00955	0.203	0.447	2.020	0.698
	5.7	21.6	0.00885	0.183	0.416	2.054	0.738
	8.2	28.5	0.00805	0.167	0.408	2.094	0.777
		30.0	0.00850	0.163	0.404	2.907	0.788
0.466	8.3	30.0	0.0161	0.333	0.577	1.794	0.478
		28.5	0.0169	0.326	0.571	1.799	0.487
	10.9	30.5	0.0130	0.324	0.569	1.888	0.489
		29.8	0.0127	0.327	0.571	1.898	0.485

### Data at 523°K (250°C)

$[c_0]$	$t$	%	$x/t$	$(c)$	$(c)^{1/2}$	$-\log \frac{x}{t}$	$-\log (c)$
0.115	1.3	15.0	0.0132	0.0974	0.314	1.879	1.011
		15.5	0.0136	0.0966	0.310	1.867	1.015
	2.0	20.0	0.0115	0.0921	0.302	1.894	1.039

		19.5	0.0112	0.0921	0.303	1.951	1.036
	3.2	33.3	0.0117	0.0766	0.273	1.932	1.116
		35.5	0.0127	0.0740	0.272	1.896	1.131
		35.7	0.0128	0.0735	0.271	1.893	1.134
	3.6	37.8	0.0119	0.0715	0.268	1.927	1.146
		38.5	0.0122	0.0705	0.266	1.914	1.152
0.229	3.2	21.4	0.0147	0.180	0.424	1.833	0.745
		20.5	0.0141	0.182	0.426	1.851	0.730
		22.0	0.0151	0.179	0.423	1.824	0.748
		22.5	0.0155	0.178	0.421	1.809	0.751
		24.0	0.0165	0.174	0.416	1.783	0.749
		23.0	0.0159	0.176	0.420	1.799	0.753
	5.6	35.0	0.0143	0.149	0.386	1.845	0.825
		32.0	0.0130	0.156	0.375	1.886	0.807
		36.5	0.0149	0.147	0.382	1.827	0.834
		37.0	0.0151	0.144	0.379	1.821	0.811
		33.0	0.0135	0.154	0.392	1.869	0.814
	8.2	40.0	0.0111	0.138	0.370	1.960	0.862
		42.0	0.0116	0.133	0.364	1.930	0.867
		41.5	0.0115	0.134	0.366	1.940	0.873
		43.0	0.0120	0.131	0.361	1.920	0.884
0.458	5.6	23.0	0.0186	0.352	0.595	1.731	0.454
		22.0	0.0178	0.357	0.598	1.750	0.447
	8.2	40.0	0.0224	0.275	0.525	1.649	0.561
		42.0	0.0236	0.266	0.515	1.627	0.575
	10.8	46.7	0.0198	0.244	0.493	1.703	0.613
		47.6	0.0202	0.240	0.490	1.695	0.620
		52.0	0.0220	0.220	0.480	1.658	0.658

Data at  $533^{\circ}$  K ( $260^{\circ}$  C)

$[c_0]$	t	%	x/t	(c)	(c) <sup>1/2</sup>	$-\log_{x/t}$	$-\log_{(c)}$
0.113	2.0	43.5	0.0251	0.0640	0.253	1.600	1.194
		45.0	0.0260	0.0623	0.250	1.584	1.206
		45.4	0.0262	0.0625	0.250	1.582	1.204
		46.7	0.0269	0.0603	0.246	1.570	1.220
		52.0	0.0300	0.0542	0.230	1.523	1.260
0.226	3.1	52.9	0.0383	0.1065	0.326	1.417	0.973
		50.4	0.0365	0.1120	0.334	1.438	0.951
		55.7	0.0404	0.1000	0.316	1.394	1.000
		56.5	0.0410	0.0985	0.314	1.388	1.008
0.452	5.6	61.0	0.0489	0.176	0.420	1.311	0.730
		59.2	0.0482	0.185	0.430	1.317	0.733
		59.5	0.0485	0.183	0.428	1.314	0.738



## Appendix B. Calibration Data

### Helium Flow--Large Capillary

pressure drop (cm)	flow rate (mmole/min)
22.6	389.4
15.1	296.3
8.8	199.3
4.6	120.0
1.0	27.3

### Helium Flow--Small Capillary

pressure drop (cm)	flow rate (mmole/min)
23.0	38.7
18.8	31.9
15.2	25.8
10.8	18.6
7.0	12.1
3.4	7.5

### Rate of Injection

Syringe Pump Dial Setting	Rate of Injection (ml/min) $\times 10^2$		
1	1.286	1.292	1.298
2	2.607	2.625	2.600
3	3.980	3.958	3.886
4	5.304	5.161	5.247
5	5.943	6.539	6.623

### Chromatographic Analysis--weight and area ratios of ethyl nitrate to t-butyl benzene

weight ratio EN/TBB <sup>a</sup>	area ratio EN/TBB <sup>a</sup>		
0.2568	0.286	0.287	0.284
0.6396	0.695	0.710	0.713
1.2689	1.450	1.460	1.450
2.6500	3.020	3.030	3.040

<sup>a</sup>EN is ethylnitrate, TBB is tert-butyl benzene.

## Appendix C. Analysis of Uncertainties

The uncertainties in the results are the maximum possible based on the uncertainties of the individual measurements. The uncertainties for the measurements and their influence on the results were estimated as follows:

1) The uncertainty of the helium flow was based on the reading of the flow meter, which could be read to  $\pm 0.6$  mm. One of the lowest readings of the flow meter was 1.2 cm. Thus, the maximum uncertainty was  $0.06/1.2 = 5.0\%$  which corresponds to long contact times. One of the highest readings of the flow meter was 20.4 cm. Thus, the minimum uncertainty was 0.3% at short contact times.

2) The uncertainty of the amount of ethyl nitrate was based on injection rate. The weight could be read from the calibration curve to 0.01 microliters/sec, which was about the limit of reproducibility. One of the smallest readings was 0.2 microliter/sec. Thus, the largest uncertainty was 5% at 0.23 mmole/l and 8 sec contact time. The smallest uncertainty was about 1% at 0.46 mmole/l and 5 sec contact time.

3) The volume of the reactor was measured to about  $\pm 2$  ml. The total volume was approximately 80 ml. Thus, the uncertainty was  $2/80 = 2.5\%$ . However, this is not a random uncertainty and will not contribute to the random

behavior of the individual values. It will be added to the final uncertainty of the rate constant.

4) The uncertainty of the gas chromatographic determination of concentration was due to the weight, which was read from the calibration curve to  $\pm 1$  mg. This was about the limit of reproducibility. One of the smallest weights was 0.1 gr. Thus, the largest uncertainty was  $10^{-3}/0.1 = 1\%$ .

5) The uncertainties of the initial concentrations were related to (1) and (2); while those of final concentrations were related to (1), (2) and (4).

Uncertainty of initial concentration-

Maximum:  $5.0\% + 5.0\% = 10\%$

Minimum:  $0.3\% + 1.0\% = 1.3\%$

Uncertainty of final concentration-

Maximum:  $5.0\% + 5.0\% + 1\% = 11\%$

Minimum:  $0.3\% + 1.0\% + 1\% = 2.3\%$

6) The uncertainties in the contact time were the same as those in the helium flow rate, since the volume of the reactor was the only other contributor and this was previously discussed in (3).

Maximum:  $5.0\%$

Minimum:  $0.3\%$

7) The uncertainties in the reaction rate constant depend on the total uncertainty in the difference between initial and final concentrations. This depends greatly on

the extent of reaction. The following calculations illustrate the problem, the data are from actual experiments.

$$\text{rate} = \text{concentration gradient} / \text{contact time}$$

$$\text{rate constant} = (\text{rate}) (\text{concentration})^{-1/2}$$

$$(a) \text{ If initial concentration } c_0 = 0.116 \text{ m mole/l}$$

$$\text{final concentration } c = 0.100 \text{ m mole/l}$$

$$t = 2.0 \text{ sec}$$

$$T = 515^\circ\text{K}$$

Since the contact time is low (high flow rates), the minimum concentration uncertainties were used.

$$\Delta C = c_0 - c = 0.116 \pm 0.116 \times 1.3\% - 0.100 \pm 0.100 \times 2.3\%$$

$$= (0.116 \pm 0.002) - (0.100 \pm 0.002)$$

$$\text{Total uncertainty in } \Delta c \text{ is } \pm 0.004/0.016 = \pm 25\%$$

$$(b) \text{ If initial concentration } c_0 = 0.458 \text{ m mole/l}$$

$$\text{final concentration } c = 0.229 \text{ m mole/l}$$

$$t = 10.8 \text{ sec}$$

$$T = 523^\circ\text{K}$$

Since the contact time is long, but the concentration high, values less than the maximum concentration uncertainties were used.

$$\Delta c = c_0 - c = 0.458 \pm 0.458 \times 8\% - 0.229 \pm 0.229 \times 9\%$$

$$= 0.458 \pm 0.037 - 0.229 \pm 0.021$$

$$\text{Total uncertainty in } \Delta c \text{ is } \pm 0.058/0.229 = 25\%$$

(c) If initial concentration  $c_0 = 0.226$  m mole/l  
 $c = 0.106$  m mole/l  
 $t = 3.1$  sec  
 $T = 533^\circ\text{K}$

Since the contact time is short, values near the minimum concentration uncertainties were used.

$$\begin{aligned}\Delta c &= c_0 - c = 0.226 \pm 0.226 \times 2.5\% - 0.106 \pm 0.106 \times 3\% \\ &= 0.226 \pm 0.004 - 0.106 \pm 0.003\end{aligned}$$

Total uncertainty in  $\Delta c$  is  $\pm 0.007/0.120 = \pm 5.8\%$

The uncertainty in a calculated value for the rate is  $25 + 0.3 = 25\%$  for low contact time and extent of reaction, and  $25 + 5.0 = 30\%$  for high contact time and extent of reaction. There is a leveling effect, since high flow rates, which correspond to low uncertainties in concentrations, produce low extents of reaction, which yield high uncertainties due to small  $\Delta c$ , and vice versa.

The third case was applicable to higher temperature experiments which yield high extents of reaction at low contact times, thus, reducing uncertainties to a minimum. The rates from these data would have an uncertainty of about 8.5%.

The rate constant calculated from any individual data point would have an uncertainty of about 30% (lower temperature experiments) to about 10% (higher temperature experiments) depending on the extent of reaction and the flow conditions.

8) The above calculations describe the maximum deviation from the mean that a data point can have under a particular set of conditions. Rate constants were calculated from each data point. From these a mean value was determined, and the standard and maximum deviations of individual values from the mean were obtained. These are tabulated below:

Temperature °K	Mean $k \times 10^2$	$\sigma \times 10^2$	Max. Dev. $\times 10^2$
515	2.5	0.4	$\pm 0.60$ (24%)
523	3.8	0.5	$\pm 0.87$ (23%)
533	11.5	1.0	$\pm 1.6$ (14%)

It can be seen that the maximum deviations fall within the range predicted from the treatment of uncertainties. In addition, the trend to more reliable values at the higher temperatures as predicted from the trend in uncertainties is observed.

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