THERMAL DECOMPOSITION OF 2-NITROPROPANE

DISSERTATION

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By

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A handwritten signature in cursive script, likely reading "Paul H. Plesch", is written over a horizontal line.

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Introduction

Review of previous work.

The vapor phase decomposition of the nitroparaffins has not been investigated in great detail. The earliest kinetic experiments were done in 1935 by Taylor and Vesselovsky,¹ who examined the

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- (1) H. A. Taylor and V. V. Vesselovsky, J. Phys. Chem., 39, 1095, 1935.
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pyrolysis of nitromethane. They found that the nitromethane decomposition obeyed essentially first-order kinetics, although it was chemically complex. They suggested $\text{CH}_3\text{NO}_2 \longrightarrow \text{CH}_3\text{NO} + \text{O}$ as the first step in the decomposition.

The photolysis of nitromethane and nitroethane vapor at 100°C was studied by Hirschloaff and Norrish,² who suggested an inter-

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- (2) E. Hirschloaff and R. G. W. Norrish, J. Chem. Soc., 1936, 1580.
-

mediate similar to the aci form found in solutions, and proposed a direct elimination of HNO to give an aldehyde.

In 1950 and 1951 the pyrolysis of nitromethane was reexamined and extended by Cottrell, Graham and Reid,^{3,4} who used pressure

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- (3) T. L. Cottrell and T. J. Reid, J. Chem. Phys., 18, 1306, 1950.
(4) T. L. Cottrell, T. E. Graham and T. J. Reid, Trans. Faraday Soc. 47, 584, 1951.
-

measurements in a static system, and carried out some product analyses. They found first-order kinetics, and an activation energy of 53.6 kcal/mole for the decomposition, and concluded that the primary step was the fission of the C-N bond; thus,
 $\text{CH}_3\text{NO}_2 \longrightarrow \text{CH}_3 + \text{NO}_2.$

The same authors extended their study to nitroethane and 1-nitropropane.⁵ Again they found first-order kinetics. The

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(5) T. L. Cottrell, T. E. Graham and T. J. Reid, Trans. Faraday Soc. 47, 1089, 1951.

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activation energies (46 kcal/mole for nitroethane and 49 kcal/mole for 1-nitropropane) were appreciably less than the C-N bond strength (57 kcal/mole) and a different mechanism was proposed. They suggested the formation of a 5-membered ring, followed by intramolecular elimination of nitrous acid, yielding the olefin and NO. Complete product analyses were not made for nitroethane, and 1-nitropropane was examined in a rather cursory manner.

Fréjacques,⁶ working at lower pressures, also examined the

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(6) C. Fréjacques, Compt. rend. 231, 1061 (1950).

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pyrolyses of the four lower nitroparaffins. He pyrolyzed nitromethane, nitroethane, 1- and 2-nitropropane in a static system and followed the reactions by noting pressure changes. He too found first-order

kinetics, but concluded from his data that the first step for all four decompositions could be represented by $\text{RNO}_2 \longrightarrow \text{R} + \text{NO}_2$, and that the products could be explained by a short chain radical mechanism.

The first work on nitromethane pyrolysis in a flow system was done by Hillenbrand and Kilpatrick.⁷ They found essentially first-

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(7) L. J. Hillenbrand and M. L. Kilpatrick, J. Chem. Phys. 21, 525, 1953.

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order kinetics and observed large amounts of formaldehyde amongst the reaction products. They felt that although their measured activation energy was close to that required to break the C-N bond, the large initial yields of formaldehyde suggested that the rate was at least in part determined by an intramolecular rearrangement.

Mueller⁸ investigated the pyrolysis of nitromethane at pressures

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(8) K. H. Mueller, J. Am. Chem. Soc. 77, 3459 (1955).

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ranging from about 10 to 18 atmospheres in sealed ampoules.

Essentially first-order kinetics were obtained and complete product analyses were made. Large amounts of hydrogen cyanide were found amongst the products, and the author felt that his data could in part be represented by a nitrogen-oxygen bond split. Thus,

$\text{CH}_3\text{NO}_2 \longrightarrow \text{CH}_3\text{NO} + \text{O}$, followed by isomerization into formaldoxime

and decomposition into hydrogen cyanide was assumed to be of importance at high pressures. The effect of added nitric oxide and nitrogen dioxide was also studied.

Gray and coworkers,⁹ in an attempt to resolve these differences

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(9) P. Gray, A. D. Yoffee and L. Roselaar, Trans. Faraday Soc., 51, 1489, 1955.

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in interpretation, investigated the pyrolyses of nitromethane, nitroethane and 1-and 2-nitropropane in a flow system at temperatures ranging from 240°C to 800°C using helium as a carrier gas. Lead, tellurium and antimony mirrors were used to detect the presence of free radicals in the decomposition products. Di-tertiary butyl peroxide was added to the nitroparaffins and sensitized the decomposition at about 200°C less than normally necessary. Formaldehyde was found to be an important reaction product. Product analyses were made for nitromethane and nitroethane; the nitropropanes were examined in lesser detail. These authors came to the conclusion that the decomposition of the nitroalkanes is a complex process, and complete interpretation was not possible. However, they felt that the carbon-nitrogen bond split, followed by short chain radical reactions could account satisfactorily for the formation of cyanides and the other observed products.

While the present research was in progress, Wilde¹⁰ published

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(10) K. A. Wilde, Ind. Eng. Chem. 48, 769, 1956.

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an account of his experiments on the vapor phase pyrolysis of the nitroalkanes in a flow system. First-order kinetics were found with respect to concentration as well as time for all cases. Some product analyses were made. Infra-red spectra showed the appropriate olefin and nitric oxide as major products; aldehydes, hydrogen cyanide and water were also found. At high temperatures and conversions methane and carbon monoxide were found; they were assumed to be formed from the oxidation of the aldehydes. For nitroethane the author felt that either a ring complex or an intermediate similar to the aci form found in solution would account for the major products; the minor products could be formed from a carbon-nitrogen split. The nitropropanes also gave first-order decompositions, and frequency factors of 10^{13} sec^{-1} were obtained. On this basis the ring complex was excluded from the considerations for them, and a unimolecular decomposition involving an activated complex similar to the aci form observed in solutions was suggested.

An error in Wilde's calculation of the rate constant for 2-nitropropane was found by this writer which, when corrected, gives a frequency factor of 10^{11} sec^{-1} for 2-nitropropane.

Experimental

Introduction

The vapor phase pyrolysis of 2-nitropropane was studied in a static system consisting of sealed sample flasks at temperatures ranging from 300°C to 340°C. A few experiments were made above 340°C, but the decomposition rate was then too high for convenient study, and the analysis of products was complicated by the decomposition of some secondary reaction products. At 250°C the rate of decomposition was slow; it amounted to 1-2% decomposition in 20 minutes, and the reproducibility was poor. The effects of changing the surface/volume ratio, and of adding nitric oxide, propylene and nitrogen dioxide were also studied.

Materials

The 2-nitropropane was supplied by the Commercial Solvents Corporation and purified by distillation at atmospheric pressure. The center fraction of the distillate had a refractive index of 1.39 at 20°C. This portion was redistilled in a small center rod column at a reflux ratio varying from 5-1 to 3-1. The constant boiling center fraction had a refractive index of 1.3942 at 20°C. The refractive index given in the Handbook of Chemistry and Physics¹¹ is 1.3941 at

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(11) Handbook of Chemistry and Physics, 37th edition, 1955-56, Chemical Rubber Publishing Co., Cleveland, Ohio.

20°C, and Toops¹² lists 1.39439 at 20°C. On this basis it was felt

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(12) E. E. Toops, J. Phys. Chem. 60, 304, 1956.

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that the 2-nitropropane was at least 99 per cent pure. Mass spectrometric analysis indicated that there was no water present in the sample, and the cracking pattern checked well with the reference pattern supplied by the Commercial Solvents Corporation. However, a small peak corresponding to about 0.06 per cent of the base peak of 2-nitropropane was found at mass 90. The identity of this impurity has not been established, and it was not possible to remove this peak from the spectra by repeated distillation. This peak was not present in the mass spectral pattern supplied by the Commercial Solvents Corporation. The purified 2-nitropropane was sealed in a container which was connected to the vacuum system via gold foil traps and a mercury cutoff, outgassed carefully and stored there for use in the pyrolyses.

Mathieson cylinder nitric oxide was passed through a potassium hydroxide trap and a liquid nitrogen trap. There it was pumped repeatedly to remove nitrogen, and then was carefully fractionated into a sample flask. Nitrogen dioxide would remain in the liquid nitrogen trap. No other nitrogen oxides or other impurities could be detected with the mass spectrometer.

Phillips research grade propylene was used without purification. Mass spectrometric analyses indicated that it contained less than 0.01 per cent propane.

Mathieson cylinder nitrogen dioxide was purified by repeated freezing and pumping to free it from nitric oxide and other materials until the solid nitrogen tetroxide was colorless. Mass spectrometric and infra-red analysis indicated no impurities greater than 0.05 per cent.

Pyrex wool was used for packing the reaction vessels to change the surface/volume ratio. It was washed with distilled water, with hot nitric acid, rinsed again with distilled water and dried. Preliminary experiments showed that this procedure did not remove solvents such as benzene and trichloroethylene which apparently were on the Pyrex wool. In subsequent experiments the carefully washed Pyrex wool was baked in an annealing oven at 600°C for several hours, and spectra obtained from the pyrolyses in which packed vessels were used showed no evidence of benzene or chlorinated materials.

The Vacuum System (Fig. 1).

The vacuum system used for this research was divided into two parts which were attached to the pumping manifold. Part A (Fig. 1) consisted of a mercury manometer which could be read to 0.1 mm., and a manifold with provisions for the filling and sealing off of six sample flasks. Gold foil traps (T) were placed between the manometer and the

manifold. The container in which the 2-nitropropane was stored was sealed on to this part of the vacuum system. Gold foil traps between the mercury float valve and the storage bulb reduced the concentration of mercury vapor in contact with the 2-nitropropane. All stopcocks in this system were greased with Apiezon T grease.

Part B of the vacuum system (Figure 1) was used for the preparation of samples which contained 2-nitropropane and nitrogen dioxide. It consisted of a container for the 2-nitropropane, a sample flask and a container for the nitrogen dioxide. All stopcocks in this system were greased with Dow-Corning silicone high vacuum grease to minimize contamination of the nitrogen dioxide.

The sample flasks were cylindrical, had volumes ranging from 38 cc to 41 cc and were equipped with a break seal and a sidearm for filling. They were baked out in an annealing oven before use.

Sample Preparation.

1. 2-Nitropropane

The following procedure was used for preparing the samples for pyrolysis. Six sample flasks were sealed on to the manifold, pumped down and the stopcocks closed. The manifold was then filled with air to a known pressure, each sample flask was opened in turn and the pressure decrease was noted. The volumes of the flasks could thus be calculated from the pressure and the volume of the manifold (94.8 cc). The system was then carefully pumped down to about 10^{-5} mm. Hg, the

flasks were flamed and allowed to cool. The 2-nitropropane, which had previously been carefully outgassed, was admitted to the line to a pressure of about 16 mm. Hg. Several minutes were allowed to establish equilibrium throughout the system. The stopcocks to the sample flasks were closed, each flask was immersed in a liquid nitrogen bath to condense the 2-nitropropane and the flasks were sealed off. The residual volume of the tubing connecting each sample flask to the stopcock was then determined in the manner described above. One sample from each filling was held out as a mass spectrometer standard.

2. 2-Nitropropane and propylene.

The sample flasks were filled with 2-nitropropane as described above. The stopcocks were closed and the 2-nitropropane condensed with liquid nitrogen. The manifold then was filled with a known pressure of propylene (8-10 mm Hg). The flask containing the 2-nitropropane was opened, the propylene was frozen into it, the stopcock was closed again and the flask was sealed off. No residual pressure of propylene could be read on the manometer. Mixtures having $C_3H_6/C_3H_7NO_2$ ratios of 1 and $3/2$ were thus prepared.

3. 2-Nitropropane and nitric oxide.

The same procedure was followed for adding nitric oxide as for adding propylene. Again no measurable pressure of the added gas

remained in the manifold after the gas was condensed into the sample flasks. The $\text{NO}/\text{C}_3\text{H}_7\text{NO}_2$ ratios varied from 1 to $1/2$.

4. 2-Nitropropane and Pyrex wool.

The packed flasks were prepared by weighing the flask, packing with glass wool, and weighing it again. From the measured diameter of the Pyrex wool (~ 0.003 mm.), the weight and the density of Pyrex the added surface could be calculated. These flasks were then filled with 2-nitropropane in the standard manner. A hundred fold increase in surface was obtained.

5. 2-Nitropropane and nitrogen dioxide.

The addition of nitrogen dioxide to 2-nitropropane was effected in part B of the vacuum system. Pure outgassed 2-nitropropane was sealed in the line, and a sample flask and the flask containing nitrogen dioxide were sealed on. The 2-nitropropane containers in part A and part B of the vacuum system were opened, and the lines and the sample flask were filled to the vapor pressure of 2-nitropropane. Since there was no manometer in part B of the vacuum system the pressure was read on the manometer in part A. The stopcock to the sample flask was closed and the 2-nitropropane was frozen. After pumping out the line, the nitrogen dioxide container was opened and manifold B was filled to a pressure corresponding to the vapor pressure of nitrogen dioxide at different temperatures. CaCl_2 -ice bath temperatures of -47.5°C , -45°C and -43°C were used which

corresponded to vapor pressures¹¹ of 4.25 mm., 5.49 mm. and 6.49 mm. Hg respectively. The nitrogen dioxide was then frozen into the flask containing the frozen 2-nitropropane. To prevent possible reactions between 2-nitropropane and nitrogen dioxide these samples were stored in Dry Ice until they were pyrolyzed.

The Furnace

The furnace in which the samples were pyrolyzed consisted of a stainless steel beaker wound with nichrome wire which was insulated with ceramic beads. A large piece of aluminum tubing was placed around the beaker and the space was packed with Santocel for insulation. The furnace was mounted on asbestos board. The salt bath consisted of a mixture of sodium and potassium nitrite. It had a temperature range from about 100°C to about 600°C and even at the highest temperature decomposed relatively slowly.

The bath was well stirred to maintain even temperature distribution. A chromel-alumel thermocouple and a Leeds and Northrop type K potentiometer were used for temperature measurements. Temperature control was manual; after reaching the desired temperature it could be maintained to within 0.1 degree by careful control of the input voltage with a Variac.

The Pyrolyses

All samples were pyrolyzed according to the following procedure. The furnace was set about 0.2 millivolts higher than the desired

temperature. The sample was immersed in the furnace, a timer was started simultaneously and the flask was clamped into position. Temperature readings were taken every 30 seconds and appropriate adjustments were made on the variac. The temperature dropped a few degrees rapidly for the first 30 seconds of the pyrolysis, but then remained at a steady value (within one-tenth of a degree) for the remainder of the pyrolysis with minor fluctuations. Because of the lowering of the furnace temperature by the insertion of a sample flask it was felt that any pyrolyses lasting less than three minutes would be subject to very serious time-temperature uncertainty, and 3 minutes was chosen as the shortest pyrolysis time. At the end of the run the samples were removed from the bath and immediately quenched in a blast of air. The removal from the furnace and placement in the air stream took about 5 seconds, the samples felt cool to the touch after about 30 seconds. In the runs made at 337°C the air quenching was augmented by immersing the samples in a beaker of ice water. The pyrolyzed samples were stored in a refrigerator until they were analyzed; the samples to which nitrogen dioxide had been added were stored in Dry Ice.

Mass Spectrometer Techniques

The mass spectrometer used in this study was a Consolidated Engineering Corporation Analytical Mass Spectrometer Model 21-103. It was equipped with a micro manometer for pressure measurements and

was modified with a high speed amplifier and a high resolution collector. This instrument had a high degree of stability with regard to hydrocarbon cracking patterns and sensitivity. A spectrum of n-butane was run daily to check the instrument performance. In the period from January 13, 1956 to July 1, 1956 the sensitivity of n-butane fluctuated about 3 scale divisions per micron about the mean value of 100 scale divisions per micron, and the 58/43 pattern coefficient deviated about 1 per cent from the mean value 12.15.

In preliminary experiments the samples were introduced into the stainless steel inlet system of the mass spectrometer by breaking the break seal with a Teflon coated smasher, and a portion was expanded into the three liter expansion volume of the mass spectrometer. Upon examination of the spectra resulting from several introductions of the same sample it was found that the peak distribution changed with time. In addition, the spectra were so complex that no identification of products could be made directly. These problems were later resolved by the following considerations.

The shift of peak distribution with repeated introductions of the same sample indicated that one or more of the components were adsorbed either on the sample flask or the inlet system. Water vapor was known to behave in this manner; it was found that 2-nitropropane also adsorbed quite strongly, and an equilibration procedure had to be devised.

The complexity of the spectra could be reduced by immersing the sample flask into various cooling baths and analyzing the non-condensable portion of the sample. Thus, the number of components in each fraction could be reduced to 5 to 10, and great simplification of the spectra was achieved. Initially five baths were used: liquid nitrogen ($\sim -196^{\circ}\text{C}$), melting Freon 22 ($\sim -150^{\circ}\text{C}$), melting Freon 11 ($\sim -110^{\circ}\text{C}$), Dry Ice and Freon 11 ($\sim -80^{\circ}\text{C}$), boiling Freon 22 ($\sim -40^{\circ}\text{C}$) and room temperature. After some experience in identification had been gained it was possible to reduce the number of fractionations to three; melting Freon 22, Dry Ice and Freon 11 and room temperature.

The presence of nitrogen dioxide in the samples to which it had been added presented special problems. Friedel and coworkers¹³

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- (13) R. A. Friedel, A. G. Sharkey, Jr., J. L. Shultz, and C. R. Humbert, *Anal. Chem.* 25, 1314, 1953.
-

have developed a direct method for the mass spectrometric analysis of nitrogen dioxide in the presence of other inorganic gases. It was necessary to condition the mass spectrometer inlet system and ion source with nitrogen dioxide or nitric acid until the mass 46 (NO_2^+) to mass 30 (NO^+) ratio was maximized and became stable, and the relative values of the peaks at mass 44 (CO_2^+), 32 (O_2^+) and 28 (CO^+ , N_2^+) reached a steady state. At this time it was presumed that no more oxidizable materials were present in the inlet system or ion

source, and routine analyses for nitrogen dioxide could be performed. Preliminary experiments indicated that this method could not be used in this research. Even with a conditioned mass spectrometer ion source, the introduction of the hydrocarbon and nitroparaffin constituents resulted in a "deconditioning" and the nitrogen dioxide cracking pattern became unstable and erratic.

Reasonably good analyses were achieved, however, by fractionating the samples. The nitric oxide which was formed during the pyrolysis appeared primarily at -150° and at -80°C . Nitric oxide in the room temperature fraction was assumed to have originated in the ion source as a result of the reduction of nitrogen dioxide, and in the calculations was assigned to nitrogen dioxide. Similarly, carbon monoxide and carbon dioxide were assumed to have pyrolytic origin in the fractions at -150°C and -80°C ; the appearance of these materials at room temperature was considered to be spurious and unrelated to the pyrolysis.

The following procedure was used for the analyses. The initial pressure of 2-nitropropane in the sample flasks was low enough so that all of the material in each flask could be used for analysis. The products resulting from the pyrolysis were fractionated from baths at -150°C , -80°C and at room temperature. In the -150°C and -80°C fractions the pressure in the expansion volume was read, the

gas was permitted to flow through the mass spectrometer for three minutes and the scan was started. The room temperature fraction contained largely water and 2-nitropropane. To insure a representative analysis the valve connecting the expansion volume and the leak was closed, and the gas was permitted to equilibrate for eight minutes (between the sample flask and the expansion volume). The pressure was read, the valve then was opened, and the standard analytical procedures were followed. This method resulted in reliable pressure readings for all three fractions, and gave reproducible analyses for 2-nitropropane and water vapor.

Vapor Phase Chromatography

Although it was possible to account for all the peaks in the mass spectra by identifying them with different materials it was thought desirable to have an independent check on the identifications. This could be done by the use of vapor phase chromatography. Mr. C. M. Drew^{14,15} has developed a gas chromatography apparatus

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(14) C. M. Drew, Chemistry Division, Naval Ordnance Test Station, China Lake, California.

(15) C. M. Drew, J. R. McNesby, S. R. Smith and A. S. Gordon, Anal. Chem. 28, 979, 1956.

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that permits the collection of the individual components, indicated by peaks on the chromatogram, for subsequent mass spectrometer

analysis and identification. Several samples were pyrolyzed in 500 ml. flasks and analyzed on a column consisting of 12 feet of coiled quarter inch copper tubing packed with 1.5 per cent squalane on Pelletex.¹⁶ A typical chromatogram is shown in

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(16) Godfrey L. Cabot, Inc., 77 Franklin St., Boston 10, Mass.

Fig. 2. The identity of the peaks, as determined by mass spectrometer analysis, is given on the chromatogram. The chromatograms did not show all of the minor components; however, all the components that were collected confirmed the previous identifications from the original mass spectra.

Figure 2. Vapor Phase Chromatogram of 2-Nitropropane Decomposition Products ($T = 329^\circ\text{C}$, 5 minutes).

Numerical Results

Treatment of Mass Spectral Data

When a substance is bombarded by electrons it may form a molecular ion by losing an electron. If the energy of the bombarding electrons be high enough, fragmentation of the molecule may result and the fragments also may become ionized. Both possibilities occur in a mass spectrometer ion source when 50 volt electrons are used. Thus each molecule has its own unique distribution of ions whose masses and abundances depend on the structure of the molecule.

The cracking pattern of 2-nitropropane is quite complex. (See Table I). The parent molecular ion at mass 89 is not detectable. The most abundant peak (base peak) is at mass 43, corresponding to the C_3H_7^+ ion. Other large peaks appear at mass 41 (C_3H_5^+), mass 39 (C_3H_3^+), mass 30 (NO^+), mass 27 (C_2H_3^+) and mass 15 (CH_3^+). This pattern complicates the calculation of kinetic results because the disappearance of 2-nitropropane cannot be followed by the change in relative abundance of the parent peak or any one peak.

The ions that occur with high probability in 2-nitropropane also are highly probable in many of the products of the decomposition. Thus, for instance, the peak at mass 43 is the most abundant peak

Table I

Mass spectrum of 2-nitropropane

<u>m/c</u>	<u>Pattern coefficient</u>	<u>m/e</u>	<u>Pattern coefficient</u>
2	0.44	40	4.88
12	0.45	41	75.53
13	0.59	42	9.65
14	2.37	43	100.00
15	10.30	44	3.54
16	0.63	45	0.09
17	0.18	46	2.63
18	0.29	47	0.03
19	0.10	48	0.04
19.5	0.06	51	0.08
20	0.11	52	0.10
24	0.03	53	0.04
25	0.39	54	0.08
26	6.13	55	0.06
27	73.95	56	0.07
28	7.83	57	0.14
29	4.25	58	0.19
30	14.64	59	0.08
31	0.59	60	0.03
32	0.09	72	0.03
36	0.10	73	0.02
37	1.86	90	0.06
38	4.39	91	0.01
39	28.86		

Standard sensitivity = $57.57 \mu/\text{div.}$
 based on sensitivity of butane = $100 \mu/\text{div.}$

for acetone, (there its nature is presumably CH_3CO^+) and is quite probable in acetaldehyde. The peak at mass 41 is the parent peak for acetonitrile (CH_3CN^+) and the base peak for propylene (C_3H_5^+). Unless very special efforts are made the ion collector cannot resolve peaks of nominally the same mass number but of different composition, and it is indifferent to the origin of the various ions. Thus, in a mixture, the various peaks represent the sums of ion contributions from different molecules, and only when the cracking patterns of all the contributing species are known can all the peaks be accounted for quantitatively.

For the precise calculation of the spectra, standard samples of all probable 2-nitropropane decomposition products were run in triplicate coincident with each set of pyrolyzed samples. Also, a flask of 2-nitropropane was saved from each filling of sample flasks and used as a mass spectrometer standard. The spectra of the standards were normalized to their base peaks, averaged, and their sensitivities determined. Sensitivity here is defined as height of the base peak per micron pressure. The sensitivities of the standard samples were referred to the sensitivity of n-butane for the day on which the standards were run, and normalized to the standard sensitivity of n-butane of 100 divisions per micron. Thus it was possible to apply the correct sensitivities over the period of several days required to analyze a series of pyrolyzed samples.

The mass spectra for the different fractions of the decomposition samples were analyzed in the standard manner. Starting at the highest mass, the more prominent peaks were considered to be the sums of the contributions from several reasonable decomposition products. The contribution of each product multiplied by its pattern coefficient was then subtracted from the spectrum. A series of successive subtractions was used until all the peaks could be accounted for completely. The base peaks of the various components were then divided by the appropriate sensitivities to convert peak heights to partial pressures. These partial pressures were summed and the total was compared with the observed pressure on the micromanometer. Pressure checks better than three per cent were obtained.

This method was followed for each fraction. To calculate the overall composition the three fractions were summed. Again, the summation of the calculated partial pressures agreed with the sum of the micromanometer readings to better than three per cent.

Since all the decomposition products arose from 2-nitropropane it was possible to check the correctness of the peak assignments in still another manner. In a correct analysis the carbon-hydrogen-nitrogen-oxygen ratio of the products should be the same as found in 2-nitropropane, that is $C_3H_7N_1O_2$. In general the carbon-nitrogen

ratios were in excellent agreement. When the value for oxygen was too low (usually about 5^o/o) it was assumed that the missing oxygen was due to water lost by adsorption. By assuming enough additional water to balance the oxygen, the hydrogen balance in general achieved the proper C₃-H₇ value.

The per cent of decomposition was calculated from the total carbon or nitrogen content of the decomposition products. When the calculations based on the two methods gave inconsistent results, greater credence was given to the values derived from carbon because the total nitrogen was subject to errors due to air leakage. Thus, the amount of 2-nitropropane that had decomposed was calculated from the decomposition products, the remaining 2-nitropropane was measured directly in the mass spectra, and the initial 2-nitropropane concentration was obtained by summing these two values.

Tabulation of Products

The numerical results of the mass spectral analyses are listed in Tables II to XI. The concentration units for 2-nitropropane are partial pressures expressed in microns and are referred to the three liter expansion volume of the mass spectrometer. The per cent decomposition is based on the disappearance of 2-nitropropane. The partial pressures of the decomposition products were converted to percentages to facilitate the comparison of various experiments.

Tables II, III and IV summarize the results for pyrolyses of pure 2-nitropropane for decompositions ranging from 4 to 51 per cent. Over this range propylene, nitric oxide and water make up between 65 and 75 per cent of the decomposition products. Acetone, acetonitrile and formaldehyde contribute between 25 to 15 per cent, so that these six materials constitute about 90 per cent of all the decomposition products. It should be noted that the relative amounts of propylene and nitric oxide remain fairly constant as a function of time, and increase only slightly with increasing temperature. This point will be discussed in more detail in another section.

Table V lists the results of pyrolyses done in flasks packed with Pyrex wool, in which the surface to volume ratio was increased a hundred fold over the unpacked vessels. Here the distribution of the decomposition products has shifted; water, acetonitrile and acetone are now the most abundant reaction products. A number of decomposition products were found that were not detected in the unpacked vessels, and there seemed to be some indication of polymerization reactions as shown by the appearance of a hexene, a hexadiene and a pentene. Visually there was no evidence of polymerization, so that its extent was probably small.

The results of the pyrolyses of 2-nitropropane-propylene mixtures are shown in Table VI. For these runs the amount of propylene formed

Table II

Pyrolyses of 2-Nitropropane at 302.5°C

Run designation	E-5	F-5	F-1
Time of decomposition	3 minutes	8 minutes	12 minutes
Percent decomposition	3.96	9.80	16.04
† 2-Nitropropane(initial)	209.77	273.77	216.33
† 2-Nitropropane(final)	201.46	246.95	181.62
† 2-Nitropropane(reacted)	8.31	26.82	34.71
† Pressure of decomposition products	25.5	72.0	92.1

Percent of decomposition products

Propylene	19.66	19.88	18.81
Nitric Oxide	21.95	23.39	21.53
†† Water	23.55	25.71	26.58
Acetone	6.51	5.22	5.17
Acetonitrile	6.84	10.54	12.25
Formaldehyde	5.49	6.13	4.11
Acetaldehyde	0.77	0.47	1.02
Nitromethane	1.70	2.47	2.39
Nitroethane	0.12	0.61	1.63
Propane	0.04	0.03	0.03
Isobutene	0.20	0.17	0.15
Ethylene	0.00	0.08	0.06
Methane	0.12	0.14	0.14
Carbon dioxide	2.34	2.21	2.38
Carbon monoxide	1.23	1.36	1.45
Hydrogen	0.12	0.07	0.05
Oxygen	3.53	0.57	0.93
Nitrogen	5.79	0.96	1.32

† Pressures expressed in microns in the three liter mass spectrometer expansion volume.

†† Water adjusted to conform with carbon-nitrogen ratio.

Table III

Pyrolyses of 2-Nitropropane at 318.6°C

Run designation	E-2	E-3	E-4
Time of decomposition	3 minutes	6 minutes	10 minutes
Percent decomposition	9.80	19.0	30.1
† 2-Nitropropane(initial)	181.44	201.77	205.40
† 2-Nitropropane(final)	163.63	163.49	143.57
† 2-Nitropropane(reacted)	17.81	38.28	61.83
† Pressure of decomposition products	45.1	100.7	160.3

Percent of decomposition products

Propylene	24.40	22.42	23.27
Nitric oxide	27.70	26.44	24.21
†† Water	23.95	24.38	25.50
Acetone	5.30	5.38	4.96
Acetonitrile	5.44	7.94	8.21
Formaldehyde	6.10	4.09	3.67
Acetaldehyde	0.36	0.63	0.91
Nitromethane	1.33	1.78	1.92
Nitroethane	0.00	1.55	1.16
Propane	0.06	0.04	0.00
Isobutene	0.32	0.26	0.26
Ethylene	0.12	0.10	0.12
Methane	0.08	0.04	0.07
Carbon dioxide	2.16	1.94	2.19
Carbon monoxide	1.08	1.23	1.54
Hydrogen	0.06	0.04	0.06
Oxygen	0.57	0.65	0.43
Nitrogen	0.95	1.09	1.50

† Pressures expressed in microns in the three liter mass spectrometer expansion volume.

†† Water adjusted to conform with carbon-nitrogen ratio.

Table IV

Pyrolyses of 2-Nitropropane at 337.1°C

Run designation	F-2	F-3	F-4
Time of decomposition	3 minutes	5 minutes	7 minutes
Percent decomposition	24.89	41.16	51.38
† 2-Nitropropane(initial)	231.28	244.63	273.44
† 2-Nitropropane(final)	173.71	143.93	132.96
† 2-Nitropropane(reacted)	57.57	100.70	140.48
† Pressured reaction products	14.8	26.0	37.2

Percent of decomposition products

Propylene	24.84	23.95	23.49
Nitric oxide	28.41	27.59	26.30
†† Water	24.02	24.82	26.47
Acetone	5.16	4.94	4.61
Acetonitrile	6.62	7.49	7.57
Formaldehyde	3.14	2.28	2.54
Acetaldehyde	1.06	1.04	0.92
Nitromethane	1.46	1.66	1.86
Nitroethane	1.24	1.48	1.19
Propane	0.00	0.00	0.00
Isobutene	0.22	0.21	0.20
Ethylene	0.17	0.22	0.22
Methane	0.07	0.07	0.07
Carbon dioxide	1.55	1.75	1.88
Carbon monoxide	1.18	1.75	2.19
Hydrogen	0.03	0.04	0.04
Oxygen	0.28	0.18	0.21
Nitrogen	0.55	0.52	0.25

† Pressures expressed in microns in the three liter mass spectrometer expansion volume.

†† Water adjusted to conform with the carbon-nitrogen ratio.

Table V

Pyrolysis of 2-Nitropropane in packed vessels

Run designation	J-2	5-GA	J-1
Time of decomposition	8 minutes	12 minutes	3 minutes
Temp., °/o decomposition	302.9 36.27	303.5 56.55	318 34.62
‡ 2-Nitropropane(initial	219.48	241.83	217.05
‡ 2-Nitropropane(final)	139.88	105.02	141.93
‡ 2-Nitropropane(reacted)	79.60	136.71	75.12
‡ Pressure of reaction prod.	199.0	346.0	190.0

Percent of decomposition product

Propylene	5.99	4.19	6.47
Nitric oxide	6.22	4.45	8.67
‡‡ Water	36.60	37.67	36.30
Acetone	9.72	10.28	9.67
Acetonitrile	20.34	20.32	19.93
Formaldehyde	0.15	0.24	0.06
Acetaldehyde	0.92	2.09	0.78
Nitromethane	1.90	1.64	1.42
Nitroethane	0.00	0.00	0.00
Propane	0.00	0.12	0.00
Isobutene	1.14	0.82	1.23
Ethylene	0.07	0.05	0.08
Methane	0.43	0.41	0.48
Carbon dioxide	5.42	5.75	5.13
Carbon monoxide	2.72	2.61	3.04
Hydrogen	0.04	0.05	0.05
Oxygen	0.14	0.13	0.08
Nitrogen	1.45	1.48	0.91
Methanol	1.27	1.05	1.13
Isopropyl alcohol	0.77	0.94	0.53
Hydrogen cyanide	2.87	3.86	1.78
Propionitrile	0.54	0.31	0.57
Acetoxime	0.88	0.64	0.80
2, 3-dimethyl-2-butene	0.40	0.56	0.51
2, 3-dimethyl-1, 3-butadiene	0.19	0.19	0.23
2-methyl-2-butene	0.14	0.15	0.16

‡ Pressures are expressed in microns in the three liter mass spectrometer expansion volume.

‡‡ Water corrected to conform with carbon-nitrogen balance.

Table VI

Pyrolyses of 2-Nitropropane-Propylene Mixtures

Run designation	K-2	K-3	K-1
Time of decomposition	3 minutes	8 minutes	3 minutes
Temperature, °C	302.8	302.9	317.8
Percent decomposed	3.48	9.47	8.26
‡ 2-Nitropropane(initial)	194.51	186.31	199.78
‡ 2-Nitropropane(final)	187.74	168.66	183.27
‡ 2-Nitropropane(reacted)	6.77	17.65	16.51
‡ Propylene(total)	233.01	327.35	316.69
‡ Pressure of decomposition products	19.2	48.6	46.1

Percent of decomposition products

‡‡ Propylene	23.78	20.25	22.13
Nitric oxide	22.79	25.18	27.29
‡‡‡ Water	28.60	24.96	24.64
Acetone	2.20	2.50	3.23
Acetonitrile	4.09	5.74	3.93
Formaldehyde	0.00	0.23	3.73
Acetaldehyde	2.78	4.21	2.73
Nitromethane	0.84	1.32	1.17
Nitroethane	0.00	0.00	0.00
Propane	0.32	0.23	0.26
Isobutene	1.26	1.65	1.06
Ethylene	1.10	1.30	1.24
Methane	0.47	0.43	0.39
Carbon dioxide	2.36	1.84	1.52
Carbon monoxide	2.82	3.12	2.45
Hydrogen	1.36	0.70	0.80
Oxygen	1.36	0.85	0.98
Nitrogen	3.88	1.14	1.19
Methanol (?)	0.00	0.37	0.22
Hydrogen cyanide	0.00	1.67	1.04

‡ Pressures are expressed in microns in the three liter mass spectrometer expansion volume.

‡‡ The propylene was computed from the nitrogen and oxygen balance.

‡‡‡ Water was adjusted to conform with oxygen-nitrogen ratio.

during the pyrolyses was computed from the nitrogen-oxygen mass balance for 2-nitropropane. These data from these experiments resemble closely those resulting from the pyrolyses of pure 2-nitropropane; the main difference was an increase in the relative concentrations of carbon monoxide, carbon dioxide and acetaldehyde at the expense of formaldehyde, acetonitrile and acetone. Isobutene, ethylene, methane and hydrogen were also increased. These effects are not sensitive to large changes in the relative propylene concentration.

The effect of nitric oxide on the distribution of the decomposition products is shown in Table VII. The nitric oxide formed in the reaction was computed to give the proper carbon-nitrogen balance. The action of nitric oxide seems to depend in a complex manner on the relative amount of nitric oxide added, on the time elapsed during the pyrolysis and on the temperature. The formation of acetonitrile and hydrogen cyanide, and of nitromethane and nitroethane is in general increased over the amounts formed from the pyrolysis of 2-nitropropane alone under similar conditions.

Table VIII shows the results for the pyrolyses of 2-nitropropane-nitrogen dioxide mixtures between 216 and 246.5 degrees Centigrade. The decomposition ranged from 1 to 2.3 per cent. As a result of this small amount of decomposition the analytical results are not very reliable. Large corrections had to be made for air, and it is

Table VII

Pyrolyses of 2-Nitropropane-Nitric Oxide Mixtures

Run designation	L-3	L-2	L-1
Time of decomposition	3 minutes	8 minutes	3 minutes
Temperature, °C	303.8	303.6	317.9
Percent decomposed	8.82	13.86	9.25
† 2-Nitropropane(initial)	211.80	352.41	777.47
† 2-Nitropropane(final)	193.12	303.55	705.59
† 2-Nitropropane(reacted)	18.68	48.86	71.88
† Nitric oxide(total found)	186.50	309.45	327.06
† Pressure of decomposition products	45.9	116.2	176.1

Percent of decomposition products

Propylene	9.25	15.51	21.24
†† Nitric oxide	5.82	10.28	16.10
††† Water	30.65	29.70	28.49
Acetone	6.01	5.12	4.25
Acetonitrile	24.08	20.91	14.53
Formaldehyde	9.16	3.14	2.40
Acetaldehyde	1.39	0.90	0.51
Nitromethane	7.14	7.64	5.17
Nitroethane	2.43	2.91	1.83
Propane	0.00	0.00	0.00
Isobutene	0.00	0.06	0.05
Ethylene	0.13	0.08	0.09
Methane	0.00	0.00	0.02
Carbon dioxide	2.80	2.60	2.10
Carbon monoxide	0.19	0.77	0.90
Hydrogen	0.13	0.05	0.06
Oxygen	0.00	0.00	0.00
Nitrogen	0.28	0.00	0.08
Hydrogen cyanide	0.52	0.32	1.24

† Pressures are expressed in microns in the three liter mass spectrometer expansion volume.

†† This quantity was calculated to conform with the carbon-nitrogen balance.

††† Water was corrected to give the proper carbon-hydrogen balance.

Table VIII

Pyrolyses of 2-Nitropropane-Nitrogen Dioxide Mixtures

Run designation	M-3	M-1	M-2
Temperature, °C	216.3	236.6	246.5
Time of decomposition	10 minutes	5 minutes	5 minutes
Percent decomposition	1.03	1.45	2.30
† 2-Nitropropane(initial)	257.98	260.88	365.59
† 2-Nitropropane(final)	255.34	257.10	357.17
† 2-Nitropropane(reacted)	2.64	3.78	8.42
† † Nitrogen dioxide	80.17	53.79	57.75
† Pressure of decomposition products	11.1	17.1	34.0
Percent of decomposition products			
Propylene	2.13	0.00 ^x	2.88
xx Nitric oxide	22.91	0.00	16.72
xxx Water	32.06	44.19	39.38
Acetone	10.66	3.99	0.32
Acetonitrile	0.00	0.00	0.00
Formaldehyde	7.90	13.03	1.35
Acetaldehyde	0.62	2.82	10.42
Nitromethane	0.53	1.88	0.24
Nitroethane	0.00	0.00	0.00
Propane	0.18	0.00	0.00
Isobutene	0.00	0.00	0.00
Ethylene	0.00	0.00	0.00
Methane	0.00	0.00	0.18
Carbon dioxide	19.10	34.10	6.65
Carbon monoxide	2.22	0.00	8.24
Hydrogen	0.27	0.00	0.15
Oxygen	0.00	0.00	0.00
Nitrogen	0.00	0.00	0.00
Hydrogen cyanide	1.06	0.00	13.14
Methanol (?)	0.36	0.00	0.00

† Pressures are expressed in microns in the three liter mass spectrometer expansion volume.

†† Nitrogen dioxide was computed: the sum of nitrogen dioxide + nitric oxide found in the -80°C and room temperature fractions.

x A very large air leak into the sample has made the product distribution meaningless.

xx Nitric oxide computed on the basis of the -150°C fraction.

xxx Water corrected to give correct carbon-hydrogen ratio.

uncertain how much of the observed oxidation process should be attributed to nitrogen dioxide and how much to oxygen. It is significant that the propylene concentration has decreased markedly, and that its possible oxidation products have increased.

Tables IX to XI show the product analyses for experiments done around 250°C. Again, the per cent of decomposition varied from 1 to 2.5 per cent, hence the analytical problems for these experiments were great and the analyses are not very reliable. It is significant, however, that little propylene was found, that acetone was the major reaction product and that acetonitrile was absent.

Calculation of Rate Constants and Activation Energies

The data listed in Tables II to XI show that in general three experiments were done at each temperature in order to determine the rate constant. The data indicate that the rate of disappearance of 2-nitropropane is best expressed by the equation for the first order decomposition

$$-\frac{d(\text{C}_3\text{H}_7\text{NO}_2)}{dt} = k(\text{C}_3\text{H}_7\text{NO}_2) \quad (1)$$

which on integration and rearrangement becomes

$$k = \frac{2.303}{t} \log \frac{(\text{C}_3\text{H}_7\text{NO}_2)_{\text{initial}}}{(\text{C}_3\text{H}_7\text{NO}_2)_{\text{final}}} \quad (2)$$

where k is expressed in seconds⁻¹. The rate constants calculated

Table IX

Pyrolyses of 2-Nitropropane at 251.3°C

Run designation	C-3	D-1	C-4	C-5
Time of decomposition(min)	5	5	8	11
Percent decomposition	1.75	1.57	1.29	2.13
† 2-Nitropropane(initial)	139.23	164.35	157.14	156.51
† 2-Nitropropane(final)	136.79	161.77	155.12	153.18
† 2-Nitropropane(reacted)	2.44	2.58	2.02	3.33
† Pressure of decomposition products	10.65	6.97	6.60	8.93

Percent of decomposition products

Propylene	2.54	5.16	3.38	6.27
Nitric oxide	17.01	21.94	23.07	16.90
†† Water	13.35	26.82	27.22	23.16
Acetone	10.43	15.63	15.84	14.57
Acetonitrile	0.00	0.86	0.00	0.00
Formaldehyde	0.00	0.00	0.00	0.00
Acetaldehyde	3.57	5.02	8.31	5.60
Nitromethane	0.01	0.00	0.00	1.34
Nitroethane	3.29	9.18	0.00	11.30
Carbon dioxide	7.24	13.05	12.30	10.07
Carbon monoxide	0.00	0.86	0.92	1.01
Hydrogen	0.38	0.29	0.62	0.45
††† Oxygen	11.75	0.00	2.92	4.36
††† Nitrogen	28.19	0.00	4.00	3.92
Diethyl ether	2.26	1.15	1.38	0.45

† Pressures expressed in microns referred to the three-liter mass spectrometer expansion volume.

†† Water corrected to give proper carbon-hydrogen balance.

††† Remaining oxygen and nitrogen after making air corrections.

Table X

Pyrolyses of 2-Nitropropane at 252.8°C

Run designation	B-2	B-4	B-5
Time of decomposition(min)	3	8	11
Percent decomposition	2.61	1.97	1.89
† 2-Nitropropane(initial)	133.86	132.71	139.59
† 2-Nitropropane(final)	130.37	130.10	136.95
† 2-Nitropropane(reacted)	3.49	2.61	2.64
† Pressure of decomposition products	8.76	6.81	7.33

Percent of Decomposition Products

Propylene	2.06	3.67	4.91
Nitric Oxide	9.49	12.19	16.37
†† Water	20.69	24.38	23.60
Acetone	22.17	20.56	18.83
Acetonitrile	0.00	0.00	0.00
Formaldehyde	0.00	0.00	0.00
Acetaldehyde	3.66	5.43	5.73
Nitromethane	0.00	0.00	0.00
Nitroethane	12.23	6.75	4.78
Carbon dioxide	8.00	9.84	9.00
Carbon monoxide	0.69	1.03	0.82
Hydrogen	0.23	0.44	0.27
††† Oxygen	10.06	4.99	6.69
††† N _i trogen	9.14	8.95	7.50
Diethyl ether	1.60	1.76	1.50

† Pressures expressed in microns referred to three liter mass spectrometer expansion volume.

†† Water corrected to give proper carbon-hydrogen ratio.

††† Remaining oxygen and nitrogen after making air corrections.

Table XI

Pyrolyses of 2-Nitropropane at 254.8°C

Run designation	D-3	D-4	D-5
Time of decomposition(min)	5	7	11
Percent decomposition	1.58	1.83	1.98
† 2-Nitropropane(initial)	174.24	170.54	156.21
† 2-Nitropropane(final)	171.49	167.42	153.12
† 2-Nitropropane(reacted)	2.75	3.12	3.09
† Pressure of decomposition products	10.12	9.30	9.09

Percent of Decomposition Products

Propylene	3.46	5.44	6.95
Nitric oxide	24.10	26.79	20.73
†† Water	22.61	23.37	25.29
Acetone	13.61	13.67	14.81
Acetonitrile	0.12	0.75	1.71
Formaldehyde	0.00	0.00	0.00
Acetaldehyde	4.15	5.23	5.01
Nitromethane	0.12	1.49	0.91
Nitroethane	9.69	7.90	6.26
Carbon dioxide	12.34	10.67	10.48
Carbon monoxide	0.23	1.28	0.80
Hydrogen	0.23	0.32	0.23
††† Oxygen	8.01	2.24	3.30
††† Nitrogen	0.00	0.00	2.85
Diethyl ether	0.69	0.53	0.57
Acetic acid	0.23	0.21	0.11

† Pressures expressed in microns referred to the three-liter mass spectrometer expansion volume.

†† Water corrected to give proper carbon-hydrogen balance.

†††, Remaining oxygen - nitrogen after making air corrections.

from equation (2) are listed in Table XII. It should be noted that the constants for the pyrolyses made at 251°C are quite scattered. For these experiments the partial pressure of all the decomposition products in the mass spectrometer expansion volume was 6 to 11 microns compared with about 160 microns of unreacted 2-nitropropane. This resulted in quite a large uncertainty in the assignment and distribution of products. Heterogeneous processes are probably also significant at these low temperatures.

It was noted previously that the amount of propylene formed per unit amount of 2-nitropropane decomposed remained virtually constant for different experiments made at the same temperature. This suggested that the formation of propylene was a first order process and might be a good possibility for the first step in the decomposition of 2-nitropropane.

To test this hypothesis a quantity b was defined, relating the concentrations of 2-nitropropane and propylene. Thus $b = (\text{2-nitropropane})_{\text{reacted}} / (\text{propylene})_{\text{formed}}$. This quantity should be constant for each temperature. The rate of formation of propylene was expressed by

$$\frac{d(C_3H_6)}{dt} = k' (C_3H_7NO_2) \quad (3)$$

which, on rearrangement becomes

$$\int_0^{(C_3H_6)_t} \frac{d(C_3H_6)}{(C_3H_7NO_2)} = k' \int_0^t dt \quad (4)$$

Table XII

First order rate constants for the decomposition of
2-nitropropane (k) and the formation of propylene (k')

T°C	k(sec ⁻¹)	b	k'(sec ⁻¹)
2-nitropropane 251°C	5.95 x 10 ⁻⁵	9.04	0.658 x 10 ⁻⁵
	5.29 x 10 ⁻⁵	7.17	0.738 x 10 ⁻⁵
	3.28 x 10 ⁻⁵	5.94	0.552 x 10 ⁻⁵
	2.69 x 10 ⁻⁵	9.18	0.293 x 10 ⁻⁵
2-nitropropane at 252.8°C	4.13 x 10 ⁻⁵	10.43	0.396 x 10 ⁻⁵
	2.85 x 10 ⁻⁵	7.33	0.389 x 10 ⁻⁵
	14.80 x 10 ⁻⁵	19.39	0.763 x 10 ⁻⁵
2-nitropropane at 254.8°C	5.29 x 10 ⁻⁵	9.17	0.577 x 10 ⁻⁵
	4.48 x 10 ⁻⁵	6.12	0.732 x 10 ⁻⁵
	3.00 x 10 ⁻⁵	5.07	0.592 x 10 ⁻⁵
2-nitropropane at 302.6°C	2.43 x 10 ⁻⁴	1.96	1.24 x 10 ⁻⁴
	2.16 x 10 ⁻⁴	1.88	1.15 x 10 ⁻⁴
	2.23 x 10 ⁻⁴	1.84	1.21 x 10 ⁻⁴
2-nitropropane at 318°C	5.97 x 10 ⁻⁴	1.61	3.72 x 10 ⁻⁴
	5.84 x 10 ⁻⁴	1.70	3.44 x 10 ⁻⁴
	5.75 x 10 ⁻⁴	1.60	3.60 x 10 ⁻⁴
2-nitropropane at 337°C	1.59 x 10 ⁻³	1.56	1.02 x 10 ⁻³
	1.77 x 10 ⁻³	1.61	1.10 x 10 ⁻³
	1.72 x 10 ⁻³	1.61	1.07 x 10 ⁻³
2-nitropropane, packed flasks, 302°C, 318°C	9.35 x 10 ⁻⁴	6.68	1.40 x 10 ⁻⁴
	11.58 x 10 ⁻⁴	9.41	1.23 x 10 ⁻⁴
	2.36 x 10 ⁻³	6.11	3.86 x 10 ⁻⁴
‡2-nitropropane- propylene mixtures 302°C, 318°C	2.02 x 10 ⁻⁴	1.55	1.30 x 10 ⁻⁴
	2.08 x 10 ⁻⁴	1.42	1.46 x 10 ⁻⁴
	4.79 x 10 ⁻⁴	1.35	3.54 x 10 ⁻⁴
Wilde's data			
367°C	4.77 x 10 ⁻³		
382°C	9.86 x 10 ⁻³		
397°C	18.66 x 10 ⁻³		

Table XII (continued)

T°C	k(sec ⁻¹)	b	k [†] (sec ⁻¹)
2-nitropropane-			
nitric oxide	5.15 x 10 ⁻⁴	4.36	1.18 x 10 ⁻⁴
mixture 302°C	3.11 x 10 ⁻⁴	2.70	1.15 x 10 ⁻⁴
318°C	5.40 x 10 ⁻⁴	1.92	2.81 x 10 ⁻⁴
2-nitropropane-			
NO ₂ mixtures			
216°C	1.66 x 10 ⁻⁵	10.99	1.51 x 10 ⁻⁶
††236°C	4.97 x 10 ⁻⁵		
246°C	7.91 x 10 ⁻⁵	8.59	9.21 x 10 ⁻⁶

† k[†] calculations based on corrected NO values.

†† No propylene found in this run.

Now, at $t = 0$

$$(C_3H_6) = 0$$

$$(C_3H_7NO_2) = (C_3H_7NO_2)_{\text{initial}}$$

and at $t = t$

$$(C_3H_6) = (C_3H_6)_{\text{observed}}$$

$$(C_3H_7NO_2) = (C_3H_7NO_2)_{\text{initial}} - b (C_3H_6)_{\text{observed}}$$

$$\text{where } b = \frac{(C_3H_7NO_2)_{\text{initial}} - (C_3H_7NO_2)_{\text{final}}}{(C_3H_6)_{\text{observed}}}$$

On integration, equation 4 becomes

$$k't = 2.303 \frac{1}{b} \log \frac{(C_3H_7NO_2)_{\text{initial}}}{(C_3H_7NO_2)_{\text{initial}} - b(C_3H_6)} \quad (5)$$

which reduces to

$$k't = 2.303 \frac{1}{b} \log \frac{(C_3H_7NO_2)_{\text{initial}}}{(C_3H_7NO_2)_{\text{final}}} \quad (6)$$

From equation 2

$$k = \frac{2.303}{t} \log \frac{(C_3H_7NO_2)_{\text{initial}}}{(C_3H_7NO_2)_{\text{final}}}$$

and

$$k' = \frac{1}{b} k \quad (7)$$

The rate constants for the formation of propylene based on equation (7) and the values of b are listed in Table XII.

Figure 3 represents a plot of the logarithms of the rate constants for the disappearance of 2-nitropropane versus the reciprocal

Figure 3. $\log k$ vs. $1/T$ for 2-Nitropropane Decomposition

of the temperature. Wilde's¹⁰ work has been included for comparison. The points for the pyrolyses of 2-nitropropane and of 2-nitropropane-propylene mixtures give a good straight line for the temperature range 302°C to 337°C. An increase in rate upon the addition of nitric oxide and upon increasing the surface is accompanied by greater scatter of the points. The scatter of the data taken at low temperatures is too great for the evaluation of a reasonable activation energy.

Figure 4 represents an Arrhenius plot of the rate constants for the formation of propylene. By this treatment the scatter in the high temperature pyrolyses has been virtually eliminated, and that of the low temperature ones has been reduced.

Figures 5 and 6 represent the results for the experiments between 302°C and 337°C plotted on a larger scale to show the consistency of the data.

The data plotted in Figure 4 (with the exception of Wilde's points) were treated by the method of least squares to give the activation energy and frequency factor for the formation of propylene.

Thus: $A = 1.11 \times 10^{11} \text{ sec}^{-1}$, $E = 39.3 \text{ kcal./mole}$.

Thus: $k = 1.11 \times e^{-\frac{39.3}{RT}} \text{ sec}^{-1}$.

Figure 4. $\text{Log } k'$ vs. $1/T$ for the Homogeneous Decomposition

Figure 5. $\text{Log } k$ vs. $1/T$ for 2-Nitropropane Decomposition

Figure 6. $\text{Log } k'$ vs. $1/T$ for Propylene Formation

Figure 6. $\text{Log } k'$ vs. $1/T$ for Propylene Formation

Discussion

Review of previous work

The relatively few studies which have been done on nitroparaffin pyrolyses have been given widely different interpretations. Fréjacques,⁶ Gray,⁹ and Wilde¹⁰ were the only authors who included 2-nitropropane in their investigations. Quantitative product analyses were not made; conclusions were based either on the rate of pressure rise or on the rate of 2-nitropropane disappearance.

Fréjacques found that his data could be best represented by $k = 2.2 \times 10^{11} e^{-\frac{39.0}{RT}} \text{ sec}^{-1}$. He noted that the dissociation energy for the carbon-nitrogen bond in 2-nitropropane was estimated as 54.5 kcal./mole.¹⁷ He felt that the carbon-nitrogen bond rupture

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(17) D. E. Holcomb and D. L. Dorsey, Jr., Ind. Eng. Chem., 41, 2788, 1949.

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was the first step in all of the nitroparaffin pyrolyses, and that subsequent chain processes could account for the observed lower activation energies. The acceleration of the decomposition rates by the addition of tetraethyl lead was considered evidence in favor of this primary split. This choice in mechanism was probably influenced by the author's results with nitromethane; here a primary split into free radicals seemed well demonstrated.

Gray and coworkers⁹ also favor a mechanism in which the primary decomposition step is the carbon-nitrogen bond rupture. The acceleration of the decomposition by methyl radicals and mirror removal during the unsensitized decomposition are given as supporting evidence for this view. The reported activation energies for nitroethane and the isomeric nitropropanes (between 39 and 50 kcal./mole) are significantly lower than the dissociation energy of the carbon-nitrogen bond. Thus, if a primary split into $R + NO_2$ is assumed, a chain reaction forming the products must be important to account for the lower activation energy.

Wilde¹⁰ on the other hand felt that the main course of the reaction (for nitroethane) was best represented by the scheme suggested by Cottrell, Graham and Reid.⁵

Presumably this step would be followed by reactions which do not involve the parent nitroethane. Some of the minor products could be accounted for by a carbon-nitrogen split and subsequent chain reactions. Wilde found that the preexponential factor in his rate constant expression was 10^{11} sec^{-1} , which indicates a negative entropy of activation if the rate determining step of the reaction be indeed unimolecular. Thus a ring complex is favored.

Similar considerations were applied to the case of the nitropropanes. For 1-nitropropane, $k = 10^{13.4} e^{\frac{-47,700}{RT}}$. The frequency factor is the normal one for a unimolecular reaction; hence Wilde excluded a ring complex on this basis. Instead he proposed an activated complex similar to the aci form of 1-nitropropane, thus $\text{CH}_3\text{-CH}_2\text{CH}=\text{N} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{OH} \end{array}$.

Wilde described the 2-nitropropane decomposition by the expression for the rate constant $k = 10^{13.0} e^{\frac{-39,000}{RT}} \text{ sec}^{-1}$. Again the ring complex was excluded on entropy considerations, a free radical split was also excluded and unimolecular decomposition was postulated. The activated complex was again suggested to have a form analogous to the aci form in solution, thus

This author has found that an arithmetic error entered Wilde's calculation of the frequency factor. In the equation $\log A = E/2.303 RT + \log k$, the $\log k$ term was inadvertently omitted. When included, the expression for the rate constant becomes $k = 1.0 \times 10^{11} e^{\frac{-39,000}{RT}} \text{ sec}^{-1}$. Thus, a ring complex would not be unreasonable.

The character of the decomposition reactions

The numerical results of this research are in good agreement with

those of Fréjacques and Wilde. The following are the expressions for the rate constants (activation energies expressed in kcal./mole)

$$k = 2.2 \times 10^{11} e^{-39.0/RT} \text{ sec}^{-1} \text{ (Fréjacques, based on the rate of pressure increase in a static system)}$$

$$k = 1.0 \times 10^{11} e^{-39.0/RT} \text{ sec}^{-1} \text{ (Wilde (corrected by T.E.S.) based on the rate of 2-nitropropane disappearance in a flow system)}$$

$$k' = 1.11 \times 10^{11} e^{-39.3/RT} \text{ sec}^{-1} \text{ (This research - based on propylene formation in a static system)}$$

Information concerning several important points in the reaction mechanism has been obtained in the present study. An Arrhenius plot of the rate constants based on the disappearance of 2-nitropropane is shown in Figure 3. The variations in rate constants at the same temperature but for different experimental conditions indicates that the reaction is partly heterogeneous. In experiments in which the surface to volume ratio was increased about one hundred fold (Δ in Figure 3) a large increase in the rate of decomposition was observed.

It is seen in Figure 4 that the scatter of points obtained for widely different experimental conditions is practically eliminated when the rate constants are based on the rate of formation of propylene. This is good evidence for the formation of propylene by a homogeneous

reaction. From equation (7), $k' = 1/b k$; thus b (ratio of 2-nitropropane reacted / propylene formed) is a measure of the degree of homogeneity. The b values (listed in Table XII) range from about 1.4 for the high temperature pyrolyses in unpacked vessels to about 6 for experiments with added surface or added nitric oxide, and are as high as 9 for some of the pyrolyses at 250°C. The variation is in the direction that one would expect; the heterogeneous reaction becomes more important when the surface to volume ratio is increased, and when the temperature is lowered.

Alternative primary steps

It then is necessary, when proposing a mechanism for the decomposition, to consider the formation of propylene as an important primary step. It is also required from the product analyses that approximately equivalent amounts of nitric oxide and water be formed for the homogeneous reaction. The rate law resulting from the proposed mechanism should indicate first order kinetics.

In the formulation of the mechanism an evaluation of different reasonable primary steps will be made in the following sections.

Primary Step (1). The energy of the carbon-nitrogen bond in 2-nitropropane has been estimated at 54.5 kcal¹⁶ and 57.6 kcal.¹⁸

(18) J. Collin, Bull. soc. roy. sci. Liège., 23, 194, 1954.

Thus, unless long chains are present, the dissociation energy is too high for the observed activation energy. The present work shows that the chains cannot be long, since neither the addition of propylene nor of nitric oxide affected the rate of propylene formation.

If $\text{CH}_3\text{CHNO}_2\text{CH}_3 \longrightarrow \text{CH}_3\text{CHCH}_3 + \text{NO}_2$ (1) be the primary step, one would expect to find some products, other than C_3H_6 , resulting from the reactions of the isopropyl radicals. Thus propane would be expected to be formed by hydrogen abstraction,

or by the disproportionation of two radicals,

Hexane would be expected from the recombination reaction,

Propylene might be formed from the disproportionation of isopropyls,

Thus, the supporting evidence is not conclusive.

Primary Step (2). - The high endothermicity of this step makes it an unlikely primary reaction.¹⁹ ΔH is estimated to be greater

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(19)	ΔH_f	Reference
O	59.1	National Bureau of Standards Circular No. 500. Selected Values of Chemical Thermodynamic Properties.
isoC ₃ H ₇ NO ₂	-33.9	Holcomb and Dorsey, ref. 17.
isoC ₃ H ₇ NO	> 19	Estimated from data on acetaldoxime given in Bichowsky and Rossini, Thermochemistry of Chemical Substances, Reinhold, New York, 1936.

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than 100 kcal.

Primary Step (3). - Spectral data do not indicate the existence of the aci form in the vapor phase. It appears unlikely that the rearrangement of CH₃CCH₃ into propylene should be quantitative, as would be required by the mass balance of the present study, where

$$(C_3H_6) \cong (NO)_{\text{corrected}}$$

Primary Step (4). - Step (4) is ruled out on the basis of energy considerations.²⁰ The heat of reaction for this process is estimated

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(20)	ΔH_f	Reference
OH	10	Gray, P. Fifth Symposium (International) on Combustion, Reinhold, N. Y. 1955, p. 535.
NO	21.6	ibid.
C ₃ H ₆	4.88	National Bureau of Standards Circular 500.
isoC ₃ H ₇ NO ₂	-33.9	Holcomb and Dorsey, ref. 17.

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at about 70 kcal.

Proposed Mechanism.

Primary Step (5). - The experimental evidence of this research favors the primary step (5), which is analogous to the one proposed by Cottrell and coworkers⁵ for the nitroethane pyrolysis. Thus,

This first step is energetically feasible.²¹ The heat of reaction for

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(21)	ΔH_f	Reference
C_3H_6	4.88	National Bureau of Standards Circular 500.
$\text{isoC}_3\text{H}_7\text{NO}_2$	-33.9	Holcomb and Dorsey, ref. 17.
HNO_2	-20	Gray, ref. 9.

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this step is thus estimated at about 20 kcal, and the only requirement for the activation energy is that it exceed 20 kcal. The observed value, 39.3 kcal./mole, satisfies this condition. The observed frequency factor, $1.1 \times 10^{11} \text{ sec}^{-1}$, suggests an entropy of activation $\Delta S^\ddagger = -10.8 \text{ e.u.}$ On these grounds a ring type activated complex is not unreasonable. The internal rotations of the nitro group and a methyl group, which contribute significantly to the entropy of this molecule, are eliminated upon the formation of a cyclic activated complex. This rearrangement would lead to a decrease in entropy.

Further evidence for the homogeneous intramolecular formation of propylene from 2-nitropropane is provided by the fact that neither the

addition of propylene or nitric oxide, nor the increased surface to volume ratio affected the rate of propylene formation.

The primary step (5-f) is then presumably followed by a sequence of reactions which account for the heterogeneous part of the decomposition. Thus, major products such as acetone, acetonitrile and formaldehyde can be accounted for by the following scheme; probably many of these steps are heterogeneous.

The NO_2 formed in (j'') or added at start of the experiment could react with 2-nitropropane,

With propylene or with formaldehyde

At low temperatures the decomposition of nitrous acid via reaction (o) must be considered

Chain termination steps such as the following may be postulated.

The experimental data show that the formation of propylene is by an intramolecular process. Furthermore, propylene is not destroyed as the reaction proceeds. Rate constants based on propylene formation are the same at 55 per cent decomposition of 2-nitropropane as those calculated at small total decompositions (4⁰/o). For these reasons reaction (j^{II}) is probably not an important one, and (m), (m^I) and (n) and (n^I) are probably only important in experiments with added nitrogen dioxide and at low temperatures.

Reactions (g) to (p^{II}) probably take place more readily on the walls than in the gas phase; this is supported by an increase in the rate of 2-nitropropane disappearance upon increasing the surface to volume

ratio, and by the increase in the relative amounts of acetone, acetonitrile, etc. over those found in the unpacked vessels.

Similarly, in the runs made at 250°C the relative amounts of products other than propylene are greatly increased. (Tables II-V, and IX-XI).

At 250°C no acetonitrile is found amongst the reaction products, and acetone is the major product. (Tables IX-XI). This result is expected from the proposed reaction scheme. The hydrogen abstraction reaction (h) should be favored over (h') at low temperatures because of the ease of abstracting the tertiary hydrogen. In addition, reaction (o) probably becomes more important than (g).

Again, the abstraction of the tertiary hydrogen by NO₂ would be favored, and reaction (o) would be followed primarily by (m), which regenerates nitrous acid. Acetone would then be produced from the rearrangement of the resulting CH₃CNO₂CH₃ via (j). As the temperature is increased the difference in the ease of abstraction of primary and tertiary hydrogens becomes less important, and the 6-fold greater probability of abstracting a primary hydrogen must be considered. Thus one would expect to find more acetonitrile at higher temperatures and this is indeed the case, (Tables II-V).

The mass balance obtained from the analytical data indicates that approximately equivalent amounts of propylene and nitric oxide are formed in the decomposition of 2-nitropropane. In the proposed mechanism, nitric oxide is formed in reactions (g) and (j). From the

product analyses it can be seen that nitrogen also is found. If one assumes the nitrogen to have been formed by the reduction of nitric oxide, and neglects all side reactions, the following relation holds for the amount of nitric oxide corresponding to the amount of propylene

$$(\text{NO})_{\text{corrected}} = (\text{NO})_{\text{obs}} + 2(\text{N}_2) - (\text{CH}_3\text{COCH}_3) \quad (8)$$

This relationship has been tested for the results of the pyrolyses between 302°C and 337°C, and the results are listed in Table XIII.

Table XIII

Comparison of observed and "corrected" nitric oxide concentrations

Run designation	NO _{observed}	NO _{corrected}	C ₃ H ₆ _{observed}
E-5	21.95	27.02	19.66
F-5	23.39	20.09	19.88
F-1	21.53	19.00	18.81
E-2	27.70	24.30	24.40
E-3	26.44	23.24	22.42
E-4	24.21	22.25	23.27
F-2	28.41	24.35	24.84
F-3	27.59	23.69	23.95
F-4	26.30	22.19	23.49

The agreement is quite good if one considers the simplifications that have been made.

It is not possible to predict the relative concentrations of formaldehyde and acetonitrile. Formaldehyde is readily attacked by oxidizing agents. The prediction of the relative concentration of acetonitrile depends on the quantitative rearrangement of the CH_3CHNO radical into CH_3CNOH (k). In experiments on the pyrolysis of nitrite esters, Levy observed increased nitromethane production when nitric oxide was added to the nitrite esters. He²² confirmed the observation²³ that the conversion of formaldoxime

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(22) J. B. Levy, Ind. Eng. Chem. 48, 762, 1956.

(23) H. A. Taylor and H. Bender, J. Chem. Phys., 9, 761, 1941.

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to hydrogen cyanide was catalyzed by nitric oxide. However, when he heated nitrosomethane in the presence of nitric oxide, nitromethane was obtained at the expense of hydrogen cyanide. Analogous processes may be occurring in the 2-nitropropane decomposition as shown by the greatly increased nitroparaffin production in experiments with added nitric oxide (Table VII).

Insufficient data are available for a detailed discussion of the reactions leading to the other minor reaction products.

Possible chain ending steps are listed in reactions (p), (pⁱ) and (pⁱⁱ). They involve the disproportionation and recombination reactions of the $\text{C}_3\text{H}_6\text{NO}_2$ radicals. The expected dimers would be difficult to

detect mass spectrometrically if present in small amounts; their vapor pressures are probably too low. The other product, 2-nitropropene, might be expected to be thermally less stable than 2-nitropropane. It would also be difficult to detect when present in small amounts, particularly in the presence of very large amounts of 2-nitropropane. These proposed chain ending steps would not significantly affect the carbon-hydrogen-nitrogen-oxygen ratio of the sum of the reaction products.

To summarize, it is proposed in this research that the thermal decomposition of 2-nitropropane proceeds via a cyclic activated complex to form propylene and nitrous acid. This intramolecular primary split is then followed by a sequence of short chains initiated by the attack of hydroxyl radicals on the parent molecule. Depending on the experimental conditions, varying amounts of acetone, acetonitrile and formaldehyde are formed as the major products of the chain sequence, which, from the observed data, can be assumed to be partly heterogeneous.

Autobiography

I, Trudy Enzer Smith, was born on May 23, 1924 in Eger, Czechoslovakia. There I attended elementary schools and gymnasium until June 1938. Upon immigration to the United States in September 1938 I attended James Madison High School in Brooklyn, N.Y. My undergraduate training was received at Greensboro College, Greensboro, N.C. which granted me the Bachelor of Arts degree (summa cum laude) in 1944. I then entered The Ohio State University. I held a University Scholarship until 1945; after that time I was an assistant in the department of chemistry. I accepted the position of research chemist at the Aerojet-General Corporation in Azusa, California, in 1950, and accepted similar employment at the Naval Ordnance Test Station, China Lake, California, in 1953. While there I completed the work for my dissertation and returned to the University to complete the requirements for the degree of Doctor of Philosophy in the Department of Chemistry.