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By

James Laurence Corey

1966

THE RADIOLYSIS OF LIQUID NITROMETHANE

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By

James Laurence Corey, B.Sc. in Chem., M.Sc.

The Ohio State University
1965

Approved by

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DEDICATION

To my parents who always had faith in me.

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There have been many people who have aided me in the work reported here. Foremost among these is Dr. R. F. Firestone, my adviser. His wide understanding of the problems involved were of great assistance. I learned much from our discussions.

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CHAPTER I

INTRODUCTION AND HISTORICAL REVIEW

Nitromethane has been the subject of many pyrolysis and photolysis studies to determine the manner by which it decomposes. Yet, the uncertainty still persists. For instance, it has been nearly 30 years since the first photolysis work,¹ but this statement recently appeared, "Further work on the determination of quantum yields and their wavelength dependence is necessary before any firm conclusions can be drawn about the mechanism of the photochemical decomposition."²

The work reported here is an attempt to shed more light (not to mention heat) on the ways in which nitromethane decomposes. There are several reasons for using ionizing radiation, gamma rays from cobalt-60 in this instance. First, to my knowledge the effect of gamma rays on nitroparaffins has not been studied before, so that some interesting comparisons and contrasts should be drawn with systems where ionizing radiation has been used. Secondly, there should be some comparisons and contrasts with the other means of decomposition.

(1) E. Hirschlaff and R. G. W. Norrish, J. Chem. Soc., 1936, 1580.

(2) M. I. Christie, C. Gilbert, and M. A. Voisey, ibid., 1964, 3147.

For a general discussion of radiation chemistry the reader should consult a text or perhaps one of the monographs in this field.³ Except where pertinent to the experimental work or to the discussion of the results a general treatment of radiation chemistry will be omitted.

An historical review of previous work on the decomposition of nitromethane can most easily be divided (like Gaul) into three parts. These are pyrolysis or thermal decomposition, photolysis, and mass spectrometry. The last category is included because of the similarities between mass spectrometry and radiation chemistry.

Pyrolysis.⁴ Taylor and Vesselowski⁴ were the first to study the thermal decomposition of nitromethane. Working with a static system in a temperature range of 390-420°C and with pressure of gas less than 200 mm they obtained nitrogen, water, nitric oxide, carbon dioxide and ethane. The stoichiometric equation is,

There was also evidence for the formation of formaldoxime, CH_2NOH . This compound is the isomer of nitrosomethane, CH_3NO . On this basis they postulated that the initial step was

(3) J. W. Spinks and R. J. Woods, "An Introduction to Radiation Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1964.

A. O. Allen, "The Radiation Chemistry of Water and Aqueous Solutions," D. Van Nostrand Co., Inc., Princeton, N. J., 1961.

A. J. Swallow, "Radiation Chemistry of Organic Compounds," Pergamon Press, New York, N. Y., 1960.

(4) H. A. Taylor and V. V. Vesselowski, J. Phys. Chem., **39**, 1095 (1935).

The other products then come from the oxidation of nitromethane and the decomposition of nitrosomethane.

The Arrhenius activation energy for the overall reaction was 61 kcal/mole.

Cottrel and Reid⁵ and Cottrel, Graham, and Reid⁶ reinvestigated the decomposition also using a static system and in the temperature range 380-430°C. Their pressure range was 200-400 mm Hg. Under these conditions they found an activation energy of about 53 kcal. From thermodynamic considerations the C-N bond strength was estimated to be about 52-3 kcal whereas the N-O bond strength was much higher. Because the estimated bond strength and activation energy were almost the same they postulated that the initial step was

Later workers have either favored reaction (2) or (5) as the initial step.

As fast secondary steps Cottrel, Graham, and Reid⁶ give,

(5) T. L. Cottrel and T. J. Reid, J. Chem. Phys., **18**, 1306 (1950).

(6) T. L. Cottrel, T. E. Graham, and T. J. Reid, Trans. Faraday Soc., **47**, 584 (1951).

Hillenbrand and Kilpatrick^{7,8} using a flow system obtained an activation energy of 50.6 kcal. Their results were in general agreement with those of Cottrel, et al. Unlike these latter workers, however, they got a large amount of formaldehyde. This suggested two additional equations.

Coupled with reaction (7) there would be a chain reaction to produce formaldehyde provided reaction (8) was slow. In a flow system the formaldehyde might be removed fast enough from the reaction zone to escape reaction (8). But, by using steady state approximations and estimated rate constants, they were able to account for only a small part of the formaldehyde produced. Finally they suggested that the formaldehyde might come from an intramolecular rearrangement such as had been postulated for the photolytic decomposition.¹

(7) L. J. Hillenbrand and M. L. Kilpatrick, J. Chem. Phys., 19, 381 (1951).

(8) Ibid., 21, 525 (1953).

Gray, Yoffe, and Roselaar,⁹ also used a flow system in which the nitromethane was greatly diluted with helium to minimize heterogeneous reactions. The temperature range was 240-800°C. They tested for free radicals with the mirror technique and also added free radical producers. The mirrors were removed and in the runs with additives a large amount of formaldehyde derivative was found. There were also strong indications of a nitrite or nitrous acid and NO₂ was a major product.

From more recent thermodynamic data than that used by Cottrell et al. ΔH for the heat of dissociation was found to be 57 kcal rather than 52-3. From the evidence that free radicals were involved Gray and his co-workers decided that a radical chain mechanism must be involved, since the heat of activation for the reaction was less than the heat of dissociation.

They were not the only ones to favor a radical chain. Earlier Frejaques¹⁰ who had worked in a pressure range of 4-40 mm Hg and in a static system had also favored a chain mechanism. Introducing tetramethyl lead at 290°C gave a chain length of 5. He also found an increase in activation energy from 40 to 46 kcal when the pressure of nitromethane was raised from 4 to 30 mm. He attributed this increase in activation energy to the introduction of at least a second chain terminating step as the pressure is raised.

Mueller¹¹ on the other hand worked at the other end of the

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

(10) C. Frejaques, Compt. rend., 231, 1061 (1950).

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

pressure scale in the range 9300-15500 mm Hg (180-300 p.s.i.a.) and at 355°C. He also made one run at 158 mm where his results were in general agreement with Cottrel et al.⁶ His results, however, were different at the higher pressures. Here hydrogen cyanide was a major initial product, along with CO, NO, and H₂O. The addition of large amounts of NO inhibited the reaction.

Hydrogen cyanide is a decomposition product of formaldoxime.

The formaldoxime can come from either the isomerization of nitrosomethane produced in reaction (2) or from,

But since NO inhibited the reaction, (13) is not important. At high pressures, then, he favored reaction (2) and at low pressures (5) as the initial step.

In this world there is always someone who is not satisfied. In 1955 appeared a paper by Makovsky and Gruenwald¹² who obtained results exactly opposite to Mueller. They found that the reaction was first order with an activation energy of 49.2 kcal and that NO did enhance slightly the formation of HCN.

They also studied the effect of other added gases. Nitrogen dioxide inhibited the reaction. Oxygen increased the rate, but reduced the HCN yield. Carbon dioxide increased the HCN yield however. Di-tert butyl peroxide which produces methyl radicals

(12) A. Makovsky and J. B. Gruenwald, Trans. Faraday Soc., **55**, 952 (1959).

caused the nitromethane to decompose at lower temperatures.

From these data equation (13) is important and equation (2) is not needed. Furthermore, equation (13) is supported by the results with CO_2 . Carbon dioxide is inert, yet by acting as a third body it increases the efficiency of the combination of CH_3 and NO .

Bradley¹³ studied the decomposition at very high temperatures by the use of reflected shock waves. He used mixtures of 90% argon and 10% nitromethane at a total pressure of 6 to 10 mm. The temperature range was 870-1190°C. The final products were CH_4 , NO , CO , and H_2O . Nitric oxide was the major product. Although the reaction remained first order the activation energy decreased to 13.7 kcal. He attributed the decrease at least partly to the formation of excited states or isomers at high temperatures.

Photolysis. Hirschlaff and Norrish¹ were the first to photolyze nitromethane. They irradiated the vapor of the refluxing liquid with a mercury lamp and from the detection of formaldehyde and other products they decided that the primary reaction was

then

(13) J. N. Bradley, *ibid.*, 57, 1750 (1961).

The overall stoichiometry is

They postulated that light absorption transforms the molecule CH_3NO_2 into the form

which then splits out NOH and formaldehyde. They estimated that 43 kcal was necessary to break the bonds.

Gray et al.⁹ in their paper on the pyrolysis of nitromethane also discussed the photolysis. They suggested that the initial step for the photolysis was also C-N bond fission. This would be analogous to alkyl nitrite decomposition where it was thought that both pyrolysis and photolysis proceed by the same mechanism.¹⁴

Brown and Pimentel¹⁵ studied the photolysis using the matrix isolation technique. Nitromethane was frozen in an argon matrix at 20°K and photolyzed with light of wavelength 2400-3600Å. They interpreted their results as indicating that the initial step was the intramolecular isomerization to methyl nitrite which then decomposes to give the observed products.

(14) J. A. Gray and D. W. G. Style, ibid., 48, 1137 (1952).

(15) H. W. Brown and G. C. Pimentel, J. Chem. Phys., 29, 883 (1958).

Later, however, Pimentel and Rollefson¹⁶ decided that the methyl nitrite could have come from the recombination of methyl radicals and NO_2 .

Nicholson¹⁷ photolyzed the gas at 27° . When the light below $2500\text{\AA}$ was filtered out, the rate of product formation was greatly reduced. He also accounted for the products formed by an initial C-N bond fission to form methyl radicals and NO_2 . Some NO_2 was then decomposed in a secondary photolysis.

Some methyl radicals were then oxidized to give the observed products.

Rebbert and Slagg¹⁸ were the only ones to study the liquid as well as the gas. They found that the major products were methyl nitrite and NO in the gas phase and CH_3ONO alone in the liquid. In the gas phase methanol and methyl nitrate were also appreciable.

For the gas phase they give the following mechanism

(16) G. C. Pimentel and G. Rollefson, work quoted in "Formation and Trapping of Free Radicals," ed., A. M. Bass and H. P. Broida, Academic Press, Inc., New York, N. Y., 1960, p. 97.

(17) A. J. C. Nicholson, Nature, **190**, 143 (1961).

(18) R. E. Rebbert and N. Slagg, Bull. Soc. Chim. Belg., **71**, 709 (1962).

At very small conversions they add,

In the liquid where methyl nitrite is the only product any excess energy can rapidly be dissipated so that methyl nitrite will be stable. They also found that the quantum yield of methyl nitrite increases with increasing temperature and decreasing wavelength of incident light. Added oxygen decreases the rate of formation of methyl nitrite. The wavelength dependence was attributed to two electronically excited states.

Bielski and Timmons¹⁹ studied the electron paramagnetic resonance spectra which occur when methyl nitrite, nitromethane, and tetranitromethane are photolyzed at 77°K. For nitromethane they found that the spectra could be explained as due to methyl radicals and NO₂. For methyl nitrite they obtained a different spectrum from nitromethane. Although the results were uncertain, they tended to favor a splitting into methoxy radicals and nitric oxide.

McGarvey and McGrath²⁰ have recently studied the flash photolysis of several compounds in the ultraviolet. When nitromethane at a pressure of 0.1 mm Hg or a mixture 10 mm CH₃NO₂/100 mm inert gas was flashed only bands due to methyl radical and nitric oxide absorption were found. No transient spectra were observed nor were OH bands when oxygen was added. No formaldehyde bands were seen under any conditions.

Methyl nitrite at similar pressures gave a formaldehyde spectrum. On the addition of a three-fold excess of oxygen the formaldehyde spectrum was suppressed and there was a weak OH absorption.

This work also supports a mechanism involving initial cleavage into methyl radicals and NO₂ with subsequent decomposition of nitrogen dioxide into NO and O.

On the other hand, Dalby²¹ observed the HNO molecule when nitromethane was flash photolyzed at pressure of 18 mm Hg. He was careful to state, however, that this does not prove HNO is one of the primary

(19) B. H. J. Bielski and R. B. Timmons, J. Phys. Chem., **68**, 347 (1964).

(20) J. J. McGarvey and W. D. McGrath, Trans. Faraday Soc., **60**, 2196 (1964).

(21) J. W. Dalby, Can. J. Phys., **36**, 1336 (1958).

products of dissociation, but only that it was formed within 40 microseconds of the start of the flash and at the particular pressure of the parent compound.

Recently the reactions of nitrosomethane have been studied. Christie, Gilbert, and Voisey² photolyzed several compounds to get monomeric nitrosoalkanes. Nitromethane and methyl nitrite were among the compounds used. The production of NO_2 when NO was added to the photolysis mixture was also studied. Nitromethane gas at 20°C and a pressure less than 10 mm was decomposed with light from an unfiltered medium pressure Hg lamp. In the absence of NO the only products were formaldehyde and nitrosomethane. With 20 mm of NO more nitrosomethane was produced than when it was photolyzed alone. But, a larger amount of NO caused the complete disappearance of nitrosomethane and the appearance of NO_2 . In discussing the photolysis of nitromethane, however, Christie and his co-workers could draw no firm conclusions as the passage quoted previously demonstrates.

Mass spectrometry. There are only two papers to report dealing with the mass spectrum of nitromethane. Kandel²² studied the positive ion spectrum and found that the most abundant ion was NO^+ . The intensity of the parent ion, CH_3NO_2^+ was 53.5%, CH_3^+ 51.6%, and NO_2^+ 35.5% of the NO^+ ion. The calculated dissociation energy of CH_3NO_2 was 2.56 electron volts. From thermodynamic data he gets 2.56 volts and from activation energies for the pyrolysis^{6,8} he gets values of

(22) R. J. Kandel, J. Chem. Phys., **23**, 84 (1955).

2.28 and 2.19 volts. From the agreement with thermodynamic data he supports C-N bond fission as the primary step

followed by

or possibly direct rearrangement

Henglein and Muccini²³ worked on the negative ion spectrum. Here the O ion is formed by 3 electron capture processes appearing at zero, 3.2, and 7.0 e.v. respectively. Thus, there is no barrier to electron capture by nitromethane.

A secondary ion is also formed

In $\text{SO}_2\text{-CH}_3\text{NO}_2$ mixtures where the capture cross section of SO_2 is much greater than nitromethane another secondary ion can be formed.²³

(23) A. Henglein and G. A. Muccini, "Chemical Effects of Nuclear Transformations," International Atomic Energy Agency, Vienna, Austria. 1961, p. 89.

Summarizing then, two possible mechanisms have been proposed as the initial step during pyrolysis.

For photolysis there are three possibilities

For mass spectrometry we have

CHAPTER II

EXPERIMENTATION

There are two ways to report the experimental procedure. The first is the logical, step-by-step approach. The second is the way things actually happened. I shall try to use the former method, although it may be necessary to lapse into the latter from time to time.

In doing this work there were a number of experimental problems to overcome and a number of pitfalls to climb out of. Therefore, I will try to describe the experimentation in as much detail as possible.

Nitromethane purification

The nitromethane was Spectroquality Reagent obtained from Matheson, Coleman and Bell. The only impurity listed on the label is 0.05% water.

To check for organic impurities gas chromatography was employed. The instrument used was a Model 609 from the F and M Scientific Corporation. This model utilizes a flame ionization detector and features linear temperature programming. Very small quantities of organic compounds can be detected in this manner.

Two columns were used. The first was 6 feet long, eighth inch diameter copper tubing. It was filled with a mixture of 5%

by weight Apiezon L grease on 60-80 mesh Chromasorb P. The mixture was prepared in the manner described by Johns.²⁴ In addition to the Apiezon L trace amounts of Alkaterge-T²⁵ and Span 80²⁵ were also added to reduce tailing of the chromatographic peaks.²⁶ The second column was 6 feet long, quarter inch diameter copper tubing. The packing consisted of 25% carbowax 20M on 45-60 mesh Chromasorb P. The first column was useful for determining the higher nitroparaffins and the second the lower boiling impurities.

The Apiezon L column was operated isothermally at room temperature. The carbowax 20M column was programmed to begin at 60°C and increase the column temperature at the rate of 3.3° per minute. Inlet and detector temperatures were maintained at 75°C.

For the Apiezon L column the flow rate of the nitrogen carrier gas was 4.0 rotameter units. From the calibration curve supplied with the instrument this corresponds to 150 ml/min. The rate for the carbowax 20M column was 6.0 rotameter units corresponding to 300 ml/min. The flow rate for both the hydrogen and the air burned in the detector chamber was also 300 ml/min.

Chromatographs of nitromethane, as it was received, revealed a number of impurities. A qualitative identification of each impurity was made by a comparison of retention times with known compounds that

(24) T. Johns, "Beckman Gas Chromatography Applications Manual," Bulletin 756-A, Beckman Instruments, Inc., U.S.A., 1959.

(25) Alkaterge-T is a trade name for a substituted oxazoline manufactured by Commercial Solvents Corporation. Span 80 is a trade name for sorbitan monoleate manufactured by the Atlas Powder Company.

(26) W. Averill, Gas Chromatography International Symposium, 3, 1 (1961), (published 1962).

were likely to be present. In this manner nitroethane and 2-nitropropane were found to be the principle nitroparaffin impurities as one would suspect from their boiling points.

There were a large number of impurities with boiling points less than nitromethane. The major low boiling impurity was propionitrile with a boiling point of 97° compared to 101° for nitromethane. Acetonitrile, acrylonitrile, ethyl nitrate, methyl nitrate, methanol, acetone, formaldehyde, methyl nitrite, ethane, and methane also occurred in lesser amounts.

The nitromethane was fractionally distilled as the first part of the purification procedure. The distillation column was 4 feet long, one inch in diameter and packed with glass beads. Three hundred milliliters were distilled at one time, the middle 150 ml being retained for further purification. Distillation was done at atmospheric pressure. Several trials at lower pressure showed no significant improvement in purification. It was interesting to note that the first few drops to distil were always cloudy and consisted mostly of water.

After the fractional distillation, the nitromethane was stored in a cool, dry, dark place until immediately prior to use. Then, it was further purified by liquid-solid column chromatography. Here it was passed through a column 25 cm long by 1 cm outside diameter. The column material was basic aluminum oxide "Woelm."²⁷ As the

(27) "Woelm" is the trade name for activated aluminum oxide manufactured by M. Woelm, Eshwege, Germany and distributed in the United States by Alupharm Chemicals, New Orleans, La. Basic Woelm has been treated to be cationotropic.

liquid passed down the column heat was generated and the oxide slowly turned from white to yellow. Examination of the nitromethane after this treatment showed that the concentrations of formaldehyde, acetone, and nitroethane had been reduced. The column described above was good for the purification of about 10 ml of nitromethane, although it took about 20 ml entering the column to get 10 ml of purified effluent.

The net result was that of the original starting material only about 25% remained after purification. It was important that the distillation be carried out before the alumina treatment. Otherwise, the water present in the nitromethane before distillation would destroy the activity of the alumina.

Table 1 shows the impurity concentrations after the treatment described above. These concentrations were obtained from calibration curves of chromatogram peak areas for known standards. The water concentration was obtained by titrating with Karl Fisher reagent. This value is an upper limit because the water concentration is so low that a more accurate determination was not possible by this method.

Having been purified, a sample was ready for degassing, transference to an irradiation vessel, irradiation, and analysis. These steps are described below, although for clarity the gamma ray source will be described first.

TABLE 1

Impurity Concentrations in Nitromethane After Treatment

Compound*	Water	Acetonitrile	Propionitrile	Acetone	Nitroethane	2-Nitropropane
Mole fraction	$\leq 1 \times 10^{-4}$	2×10^{-4}	4×10^{-3}	4×10^{-5}	7×10^{-5}	3×10^{-4}

* Other impurities originally present in starting material were below detectable limits.

Gamma ray source

Briefly, it is a capsule containing cobalt-60 rated at 205 curies in April, 1963. The capsule is attached to a long rod which can slide up and down. When not in use, the rod is in the up position, held by a shutter mechanism, and sits in a lead container on wheels. In use the container is moved over a pit surrounded by lead and concrete. When the shutter is opened the rod can be lowered into the pit. A sketch of this arrangement is shown in Figure 1.

The sketch also shows that when the source rod is lowered, it slides into a tube in the pit. Around this tube may be placed a bath to control the temperature. Thus, the tube serves a dual purpose. It protects the source capsule from the bath and it serves as a centering post for vessels to be irradiated.

Irradiation vessel

The "basic" irradiation vessel is shown in Figure 2, along with some attachments. It is made of Pyrex glass, annular in shape, and holds slightly more than 5 ml of liquid. An annular vessel was employed to make the most efficient use of the gamma rays coming from the cylindrical capsule. The purpose of the various attachments to the radiation vessel will be discussed in the sections dealing with analysis.

Preparing a sample for irradiation

Before a sample was irradiated, it had to be degassed and transferred to the irradiation vessel. Five milliliters of

Figure 1.-- End view of cobalt -60 container and source pit.

Dimensions:
 outer diameter
 35 mm.
 height
 31 mm.
 inner diameter
 21.7 mm.

Basic radiation vessel

Break - seal

Break-seal and
residue bulb

Pull-off tubes

One centimeter
optical cell

Figure 2.--The radiation vessel and attachments

purified nitromethane were pipetted into a glass bulb with a standard taper joint. Anhydrous calcium sulfate was added as a drying agent. The bulb was then placed on the vacuum line as shown in Figure 3. All joints and stopcocks were lubricated with Dow Corning silicone, high vacuum grease. The nitromethane was then frozen with liquid nitrogen. When the stopcock to the pump was opened, the uncondensed gas was removed. Next, the stopcock was closed and the nitromethane melted. Dissolved gas escaped from the liquid. The nitromethane was refrozen and the cycle repeated. After the third cycle and with the nitromethane still frozen in the bulb, the rest of that part of the vacuum line was heated with a torch to drive off adsorbed gas. The radiation vessel received special treatment because it is rather delicate. After cracking several vessels while using the torch on them, a new method of heating was adopted. A small electric oven just large enough to fit around the vessel was used to heat it just below the softening point of the glass. After maintaining this temperature for about an hour, the vessel was slowly cooled. No vessel treated in this way cracked, although in two instances the vessel was overheated. When that happened the external pressure and internal vacuum (the line was pumped on during heating) caused the glass to suck in, ruining the vessel. After the line had cooled to room temperature, the nitromethane was melted and vacuum distilled into the irradiation vessel. Here it underwent two more freeze-thaw cycles. After a total of three cycles no more gas could be seen to escape from the melt. Five cycles including the two in the irradiation vessel were used to be on the safe side.

Figure 3-- Nitromethane degassing system including Nitrogen dioxide purification system.

After the fifth cycle, the nitromethane was frozen and the vessel was sealed off and removed from the vacuum line using the gas-oxygen torch. When the hot glass had cooled and the nitromethane had melted, the five milliliter sample was ready for irradiation.

Preparation of solutions

Several experiments were run to study qualitatively the effect of additives. In one a small amount of water was added to the nitromethane before irradiation. In another gaseous nitrogen dioxide was dissolved and the solution irradiated.

The solution of water in nitromethane was prepared as described above except that no drying agent was used. The solution of NO_2 in nitromethane was more difficult to make.

For the preparation of such a solution it was necessary to add to the vacuum line the portion shown within the dotted lines in Figure 3.

The source of NO_2 was a cylinder from the Matheson Company. The gas was practical grade and contained a number of impurities including nitrogen and nitric oxide.

After the nitromethane was degassed and transferred to the irradiation vessel, that portion of the line was closed off. Then, the impure NO_2 was introduced through the phosphorus pentoxide drying tube. The gas was condensed in the traps to a blue solid at -196°C . The stopcock to the vacuum line was opened and the non-condensable gas was pumped off. This stopcock was closed and the solid was warmed to give the gas again. Next, industrial grade oxygen was introduced to oxidize the nitric oxide present to the

dioxide. The dioxide was refrozen and unreacted oxygen was pumped off. This process was repeated several times until the solid no longer showed any blue color. Then, the gas was frozen at -78°C and any gases present at this temperature were pumped off. This removes nitrous oxide and carbon dioxide.

The purified gas was allowed to enter the portion of the line containing the nitromethane. When the nitromethane was frozen at -196°C , the dioxide also condensed. The irradiation vessel was sealed off and removed from the vacuum line. The solution of NO_2 in nitromethane was yellow and apparently stable, since no change in absorbance was observed on a spectrophotometer when the solution was allowed to stand for a day.

Irradiation

The irradiation procedure itself was quite simple. The vessel was placed so that it rested around the base of the centering tube in the source pit. A thermocouple was placed nearby to measure the temperature. The source and its shielding were moved into place, driven by an electric motor (not shown in Figure 1). After noting the time, the source rod was lowered. Later the operation was repeated in reverse and the sample removed for analysis.

Qualitative gas analysis

The analysis of the radiolysis products proved to be the most difficult and challenging part of this work. One can see from the historical review that a large number of products are possible, and that they may occur in any state, gas, liquid, or solid.

Preliminary experiments showed that gas was indeed produced. So in addition to a vacuum line for preparing samples, another was built to measure the volume of gas produced. This is the reason for the break-seal attachment on the irradiation vessel. The gas measuring system is shown in Figure 4, and is of the usual type for this kind of work.

After an irradiation the vessel was sealed to the line as shown in Figure 4. Then, the system was evacuated. When the McLeod gauge showed that the pressure had been reduced to 10^{-5} mm Hg, the gas measuring part of the line was closed off from the vacuum line. The seal was then broken, and the gaseous products and nitromethane vapor passed into the analytical system.

Before the gases entered the Toepler pump they passed through two traps. The traps were cooled in such a way as to allow fractional distillation of the products while preventing the passage of nitromethane as much as possible. From the Toepler pump the gases passed into the gas buret where the volume was measured.

For the initial qualitative analyses the gas was pushed into an infrared gas cell and the fractions collected at the several temperatures examined to see what might be the products. To get enough gas to give large peaks in the infrared it was necessary to irradiate for 60 hours at room temperature. A Perkin-Elmer Model 237 instrument was used to obtain the spectra. In this way the following compounds were observed, methyl nitrite, nitric oxide, nitrous oxide, methane, ethane, carbon monoxide, carbon dioxide, formaldehyde, and also

Figure 4.-- Collection system.

possibly, hydrogen cyanide, although the latter compound was not observed for runs of six hours or less.

Gas chromatography was employed to look for additional gases that might not appear in the infrared and to confirm the presence of those compounds that were observed. Hydrogen and nitrogen were found in this manner.

Many of the gases listed above cannot be detected by flame ionization. Instead, an Aerograph Model A-350-B, which is a thermal conductivity instrument, was used. This is a dual column instrument with temperature programming. Hydrogen and nitrogen were found on a molecular sieve 5A column at 100°C. Methane and carbon monoxide were also confirmed on this column. No oxygen was found. Nitric oxide, N_2O , CO_2 , CH_3ONO , and C_2H_6 were confirmed, on a 10 foot, quarter inch diameter column of 25% Apiezon T on 60-80 mesh Chromasorb P. Nitric oxide was also confirmed on a silica gel column. This silica gel column will be discussed in more detail in the next section. Formaldehyde and methyl nitrite were also confirmed with the carbowax 20M column on the flame detector instrument.

Quantitative gas analysis

Once the gaseous products were known the next step was to get quantitative results. Mass spectrometry was a possible method, but the many products and their complicated mass spectra ruled out this method. Gas chromatography appeared to be more feasible as indicated by the data from the qualitative analyses.

The procedure was as follows: Two fractions of gas were collected, the first at -196°C and the second at -80°. The first

fraction consisted entirely of hydrogen, nitrogen, methane, and carbon monoxide. The remaining gases came over in the second fraction, along with traces of the gases listed above and not entirely collected in the first fraction.

After the volume of the first fraction was measured, it was pushed into the bulb shown in Figure 5. The bulb is closed with a stopcock at one end and a rubber septum at the other. With the stopcock closed the bulb was removed from the line and brought to the gas chromatograph. The sample inside the bulb was usually at considerably less than atmospheric pressure. A gas syringe jabbed through the septum would cause a small amount of air to enter the bulb. An even larger amount would have entered when a sample was withdrawn in the syringe. This source of error was overcome by filling the exterior volume of the bulb with mercury, and setting it into a U-tube of mercury. When the stopcock was opened, mercury entered the bulb until the pressure was equalized. A small excess of mercury was then added to the U-tube. This caused a slight positive pressure inside the bulb, and reduced the possibility of air entering the bulb when the needle of the syringe was inserted through the septum. When gas was withdrawn the mercury level rose to replace the gas.

The gas chromatography column used for the separation of the four gases collected at -196°C was 10 feet long, 7 mm in outside diameter and made of Pyrex glass, rather than copper as in the other columns used in this work. It was filled with 80-100 mesh silica gel and was similar to the one described by Marvillet and Tranchant.²⁸

(28) L. Marvillet and J. Tranchant, "Gas Chromatography 1960," R. P. W. Scott, ed., Butterworth Inc., Washington, D. C. p. 321.

Figure 5.-- Gas sampling bulb and pressure equalizer.

The column was operated at room temperature. The carrier gas was helium at a flow rate of 30 ml/min. This column gave a good separation for the gases collected at -196°C . In fact at room temperature it is possible to partially separate air into nitrogen and oxygen on the column.

For this quantitative work calibration curves of peak area versus moles of gas were plotted. In general sensitivity correlated with thermal conductivity. Thus, the instrument was forty times less sensitive to hydrogen than nitrogen, because hydrogen's thermal conductivity is very close to that of helium.

When we come to the fraction of gas collected at -80°C , it is easy to see why Nicholson¹⁷ did not analyze it quantitatively, for there are some grave difficulties involved. In the first place at -80°C the vapor pressure of nitromethane is high enough so that some will be introduced into the gas buret with every cycle of the Toepler pump. If enough is introduced condensation of liquid nitromethane will take place which interferes with the volume measurement. Secondly, formaldehyde vapor, which was also present, tends to polymerize on the walls. Thirdly, should any NO_2 be present, it would be converted to nitric oxide and other products by the mercury in the Toepler pump and gas buret.²⁹ (The possible presence of NO_2 was a source of considerable anxiety, and it was not until much later that the writer was able to show by another method that NO_2 , if present at all, is there in very small amounts.) Finally, the fourth difficulty is

(29) E. S. Freeman and S. Gordon, J. Am. Chem. Soc., **78**, 1813 (1956).

the solubility of methyl nitrite and formaldehyde in nitromethane. Even by melting the nitromethane to allow gas to escape and then refreezing at -78°C , which was standard practice, it was impossible to remove all these gases in a "reasonable" length of time.

Once the gas was collected, measured and transported to the gas chromatograph there were other problems with which to contend. The gas mixture could not be entirely analyzed on one column, thus making it necessary to depend on absolute calibration. That is, when a mixture can be measured on one column, it is possible to compare the calculated volume obtained on the basis of peak areas with the volume injected, and thus to normalize the results. When two or more columns are needed this normalization is not possible. Furthermore, the need for two or more columns reduces the accuracy because smaller volumes must be injected. For example, in a one milliliter gas syringe one can measure a volume to about ± 5 microliters. For a 100 microliter sample this is a 5% uncertainty but when two 50 microliter samples must be used for two columns the uncertainty is 10% for each injection.

Nitric oxide in the mixture also increases the difficulty of analysis because of its reactivity.²⁸ The silica gel column must be absolutely clean and dry. Should any air be in the syringe or get into the sample, the NO would be converted to NO_2 . That is why the analysis for NO is the least accurate of the gases that were measured on the thermal conductivity gas chromatograph.

Dark reaction

It was not long after the gas analyses began, that a strange phenomenon became apparent. The amount of gas collected from irradiations done at 25° depended on the time before analysis began. In other words a reaction continued even after the nitromethane was removed from the gamma ray source. Such reactions although uncommon in radiation chemistry are by no means unknown. The nature of this dark reaction will be discussed later.

In terms of the analysis procedure an irradiated vessel had to be analyzed immediately after removal from the source pit. All vessels were analyzed within twenty minutes of their removal, and during this time they were kept at 0°C which slowed down the dark reaction. Several experiments showed that under these conditions a vessel irradiated for six hours at 25° and then chilled to 0° did not show an increase in gas volume within experimental error for at least two hours.

Liquid analysis

As much gas as possible was removed, and the liquid nitromethane was vacuum distilled into a bulb which was sealed off and removed for analysis on the flame ionization chromatograph. A comparison with a blank run showed that impurity concentrations had not changed. The irradiated liquid, however, showed additional peaks. Two peaks were due to methyl nitrite and formaldehyde which were not completely removed in the gas analysis. In addition to these peaks a third was identified as methyl nitrate. Methanol was not found.

It was now necessary to find another method for the analysis of methyl nitrate and formaldehyde. Moreover, a method was sought which would not require opening the vessel, so that several measurements might be made on one run. An optical method was a possibility. Unfortunately, nitromethane was a most unpromising solvent for products. The liquid absorbs light almost completely at wavelengths shorter than $3800\overset{\circ}{\text{\AA}}$. Moreover, none of the products absorbed in the visible region. The infrared would have required sodium chloride windows so that fabrication of a workable union of irradiation vessel and infrared cell might have presented problems. Also, nitromethane absorbs very strongly in several regions of interest. All in all an optical method did not look hopeful.

Methyl nitrite, though, shows some slight absorption out to $4000\overset{\circ}{\text{\AA}}$. By using pure nitromethane as the reference liquid rather than water, it was possible to go down to $3700\overset{\circ}{\text{\AA}}$ on a Bausch and Lomb Spectronic 505 double beam spectrophotometer before the reference energy dropped to zero. The absorption is shown graphically in Figure 6.

Methyl nitrite was prepared by the action of sulfuric acid on a solution of methanol, water, and sodium nitrite. It was dried by passage over anhydrous calcium chloride and phosphorus pentoxide and purified by bulb to bulb vacuum distillation. The ultraviolet spectrum is the same as that found by Yoffee and Gray³⁰ and Tarte.³¹

(30) A. D. Yoffee and P. Gray, J. Chem. Soc., **1951**, 1412.

(31) P. Tarte, J. Chem. Phys., **20**, 1570 (1952).

A. Nitromethane liquid

B. Methyl nitrite gas

C. Methyl nitrite dissolved in Nitromethane

Figure 6.-- Ultraviolet spectra of Nitromethane and Methyl nitrite.

Qualitative tests of methyl nitrite dissolved in nitromethane with pure nitromethane as the reference liquid showed that the differential absorption of methyl nitrite could be followed down to $3750\text{\AA}$. Below this wavelength the light intensity reaching the photocell was too weak to detect the absorption due to methyl nitrite. This also is shown in Figure 6.

The spectrophotometer cell attachment is shown in Figure 2. Fused silica was used as the cell material because it does not become colored as rapidly as many glasses when bombarded by gamma rays. The optical cell was joined to the vessel through a graded quartz to Pyrex seal.

The next step was to determine the extinction coefficient for gaseous methyl nitrite at some wavelength and then for methyl nitrite dissolved in nitromethane at $3750\text{\AA}$. To do this the special cell shown in Figure 7 was built. Methyl nitrite at a known pressure and temperature was introduced into the cell. From the ideal gas law the concentration was calculated. Next the absorbance was measured over the wavelength range $3000\text{--}4100\text{\AA}$. The absorbance was obtained for several different vapor concentrations. From a Beer's Law plot of absorbance against concentration the extinction coefficient was determined to be 50.2 liters per mole cm at $3650\text{\AA}$. This value is in general agreement with the extinction coefficients for other nitrites.^{32,33}

(32) R. N. Haszeldine and B. J. H. Mattinson, J. Chem. Soc., 1955, 4172.

(33) A. P. Altshuller, I. Cohen, and C. S. Schwab, J. Phys. Chem., 62, 621 (1958).

Figure 7.--Device used to obtain extinction coefficients for Methyl nitrite in the gas phase and in Nitromethane liquid.

After the absorbance of the gas had been measured, 5.0 ml of nitromethane was injected through the rubber septum. The cell was shaken to dissolve the methyl nitrite and the absorbance was measured at $3750\text{\AA}$. It was assumed that all the methyl nitrite was dissolved. This assumption was checked in several instances by observing the spectrum of the vapor above the liquid. When the initial concentration of methyl nitrite was less than 0.012 moles/liter the assumption was valid. This is seen in the Beer's Law plot in Figure 8. The extinction coefficient is 38 liters/mole/cm at $3750\text{\AA}$ for methyl nitrite in nitromethane at 27°C .

Several runs made at both zero and 25°C showed that the absorbance was linear with absorbed dose of gamma rays. On the assumption that all the optical absorption at $3750\text{\AA}$ was due to methyl nitrite, the yield of that compound was almost ten times the yield obtained from the gas analyses for a given dose of gamma rays. It was highly unlikely that the gas runs could be that much in error, so another explanation was sought.

One possibility was that one or more other products might also absorb at that wavelength. There are a number of compounds containing the N-O group that do absorb in the region of $3750\text{\AA}$. Several experiments showed that this was indeed happening.

So, another method was sought which would give the methyl nitrite concentration in irradiated nitromethane unambiguously. Yet, the optical method was not a complete failure as we shall see.

The method which was finally successful was the "pull-off"

Figure 8.--Determination of the extinction coefficient for Methyl nitrite in Nitromethane at 3750 angstrom units and 27°C.

technique. In this method a side arm having several small tubes attached was joined to the irradiation vessels as shown in Figure 2. After the liquid in the vessel had been irradiated for a given time, the vessel was removed from the pit. Then, it was tilted so that a small quantity of the liquid went into one of the tubes. Both vessel and tube were cooled with liquid nitrogen so that the liquid in each froze. Next the tube was heated with a torch and pulled off. The vessel was warmed to melt the nitromethane and put back in the pit. After the heated tip of the pull-off had cooled and the nitromethane had melted, the sample was ready for analysis on the flame ionization detector gas chromatograph.

The glass was thick at the end where the tube was pulled off (see Figure 2). By breaking the tube at the tip where this thick glass causes the tube to narrow, it was possible to get a tiny orifice just large enough for the insertion of a needle of a ten microliter liquid syringe. After the syringe was withdrawn, the hole was capped with a drop of melted sealing wax, so that a second sample could be removed without losing dissolved gas. Several experiments showed that this method gave reproducible results.

The big advantage of this method was that it permitted the analysis of formaldehyde as well as methyl nitrite. The method does have several possible drawbacks, however. Pyrolysis may occur when the side tube is heated to pull it off. Secondly, there may be fractional distillation when the tube and vessel are cooled; that is, the liquid in the side tube tends to cool faster than in the vessel. This would lead to fractional distillation of the more

volatile products into the side tube. Finally, there is the possibility that some methyl nitrite and formaldehyde are lost when the side tube is opened to insert the syringe needle.

Pyrolysis was avoided by careful handling and a very small flame. Fractional distillation was reduced by cooling the vessel to almost the freezing point of nitromethane before transferring liquid to a side tube.

The optical method was used to check the third source of error. The method had been discarded because of interference from other radiolysis products, but it was later found that the interfering products were nonvolatile. In other words the methyl nitrite could be analyzed by vacuum distilling the irradiated nitromethane into an optical cell, leaving the interfering products behind.

Although a tedious procedure, here was a comparison with the results of the "pull-off" technique. Furthermore, here was a way to determine whether NO_2 was present or not. Nitrogen dioxide is volatile and absorbs at $3750\overset{\circ}{\text{A}}$. If it were present in large amount, the result of the optical analysis would show much more apparent methyl nitrite than the pull-off method, since NO_2 is not detected by the flame ionization gas chromatograph but does absorb light in the vicinity of $3750\overset{\circ}{\text{A}}$.

One optical experiment was run in which the liquid was vacuum distilled into an optical cell after irradiation. The result is shown in Table 4 and Figure 13. Within experimental error NO_2 was not a product.

Residue analysis

As mentioned above, when nitromethane was irradiated and then vacuum distilled, a residue was left behind. Usually it was left as a yellowish oil, although occasionally a solid was deposited. Others investigating nitromethane decomposition have also seen a residue. Nicholson,¹⁷ for example observed a white residue which he thought was a mixture of formaldehyde and formaldoxime polymers.

At first the residue found in the present work was also attributed to the same cause, especially since the residue gave a positive test for formaldehyde or formaldoxime with chromatropic acid. Most attention was focused on the gaseous products.

Later, after studying the work that had been done on nitroso-methane³⁴⁻³⁶ and its dimers, the writer decided to give the residue another look. It was a great thrill to observe that the residue gave a positive Leibermann nitroso test. The residue was partly soluble in water, and the ultraviolet spectrum of the solution showed a peak at 265 mμ.³⁵ An infrared spectrum of the residue was compared with that of pure cis-nitrosomethane dimer which was very kindly supplied by Dr. B. G. Gowenlock.³⁷ The spectrum showed the presence of the cis dimer, and, in addition, there were other compounds.

Once the presence of the dimer was established, it remained to determine it quantitatively. A bulb which would hold five milliliters

(34) H. T. J. Chilton, B. G. Gowenlock, and J. Trotman, Chem. & Ind., 1955, 538.

(35) B. G. Gowenlock and J. Trotman, J. Chem. Soc., 1955, 4190.

(36) B. G. Gowenlock, H. Spedding, J. Trotman, and D. H. Whiffen, ibid., 1957, 3927.

(37) B. G. Gowenlock, Chemistry Department, University of Birmingham, Birmingham, England. Private communication.

of nitromethane was attached to the radiation vessel along with a break-seal as shown in Figure 2. After an irradiation, the liquid was vacuum distilled from the bulb leaving the residue. Transferring from the bulb rather than the irradiation vessel was simply a matter of convenience, because it is easier to handle the residue when it is in the bulb.

After all the liquid had been removed from the bulb, the system was opened to the air and the bulb removed from the line. Then, the bulb was smashed and the contents dissolved in a known volume of water. From the published extinction coefficient³⁵ and the assumption that the absorption at 265 m μ was entirely due to the dimer the concentration of the dimer was calculated. The validity of this assumption will be discussed in another place.

Usually, not all the residue was water soluble. A small amount of white residue was sometimes left that gave a positive chromotropic acid test. When enough of this material was scraped up after several runs, it gave an infrared spectrum of formaldoxime trimer. The oxime was not determined quantitatively.

Dosimetry

In radiation chemistry as in photochemistry one must know the rate of energy input into the system under consideration. In photochemistry this leads to quantum yields whereas in radiation chemistry G-values are the result. The G-value for a product of radiolysis is defined as the number of molecules of product formed per 100 electron volts absorbed by the system. For decomposition

the G-value is similarly defined as the number of molecules decomposed per 100 e.v. absorbed.

The next question, then, is how to measure the energy input. Fortunately, there exist dosimeters for which the G-values are known. For the radiolysis of liquids perhaps the best known is the Fricke dosimeter. Here the G-value for the oxidation of ferrous to ferric ion in aqueous solution was determined.

In the present work 5 milliliters of the dosimeter solution, prepared according to the recipe given by Lind³⁸ was pipetted into an irradiation vessel. Then, the dose rate was found. From the rate in the aqueous solution and the usual assumption that the energy absorption is proportional to electron density, it was possible to calculate the dose rate in nitromethane.

As an example the dose rate in the Fricke dosimeter was 9.0×10^{17} electron volts per gram minute on October 15, 1964, for a particular vessel. The electron density in the solution is 3.42×10^{23} electrons/ml.³⁹ For nitromethane we have

$$\frac{32 \text{ electrons}}{\text{molecule}} \times \frac{6.023 \times 10^{23} \text{ molecules}}{\text{mole}} \times \frac{1 \text{ mole}}{61.04 \text{ grams}} \times \text{density,}$$

or

$$3.16 \times 10^{23} \text{ (electrons/g)} \times \text{density.}$$

The density of nitromethane at 25°C is 1.13 g/ml, and at 0° it is

(38) S. C. Lind, "Radiation Chemistry of Gases," Reinhold Publishing Corp., New York, N. Y., p. 59.

(39) H. R. Werner, Ph.D. dissertation, Western Reserve University, Cleveland, Ohio, 1963, p. 53.

1.16 g/ml. Therefore, the dose rate at 25^o C was 9.0×10^{17} x
 3.16×10^{23} x $1.13/3.42 \times 10^{23} = 9.4 \times 10^{17}$ e.v./gm of nitromethane.
At 0^oC the rate was 9.7×10^{17} e.v./gm.

CHAPTER III

EXPERIMENTAL RESULTS

Gases

The gaseous products were the first to be determined quantitatively, so that a typical calculation for gas yield will be given first. Run No. 19 was for four hours at 0°C. The volume of gas collected in the gas buret was 0.321 cc at 1.00 atmosphere and 28°C. The percentage composition by volume found on the gas chromatograph was nitrogen 35.8%, hydrogen 26.8%, carbon monoxide 27.8%, and methane 9.6%.

The moles of nitrogen collected were calculated from the ideal gas law,

$$\text{moles of N}_2 = \frac{0.358 \times 0.321 \text{ cc} \times 1.00 \text{ atm.}}{(273+28) \times 82.05 \frac{\text{cc atm.}}{\text{mole deg.}}} = 4.56 \times 10^{-6} \text{ moles}$$

Next this was converted into mole fraction. Because the conversion of nitromethane into products is very small, the nitromethane may safely be considered as the only compound contributing to the denominator in the equation,

$$\text{mole fraction of product} = \frac{\text{moles of product}}{\text{total moles present}}$$

Five milliliters of nitromethane at an original temperature of 25° was always used, even though it may have later been cooled to 0° for an irradiation. Hence the number of moles of nitromethane was

$$\frac{5.0 \text{ ml} \times 1.13 \text{ g/ml}}{61.04 \text{ g/mole}} = 0.0926 \text{ moles}$$

The mole fraction of nitrogen collected from Run No. 19 was $4.56 \times 10^{-6} / 0.0926 \times 10^{-1}$ or 5.0×10^{-5} . The mole fractions of the other gases were calculated in the same way.

It was also necessary to calculate the dose of gamma rays absorbed by the nitromethane during the run. The dose rate at 0° and in the vessel used for Run No. 19 was 8.8×10^{17} e.v. per gram per minute. Thus, the absorbed dose was

$4.0 \text{ hr.} \times 60 \text{ min/hr} \times 8.8 \times 10^{17} \text{ e.v./g.min} \times 61.04 \text{ g/mole},$
or $12.8 \times 10^{21} \text{ e.v./mole}$. In this manner the values given in Tables 2 and 3 were calculated.

Liquid solutions

For methyl nitrite, formaldehyde and methyl nitrate, the situation is somewhat different, since these compounds were determined on the gas chromatograph as solutions in nitromethane. For example, the calibration factor for methyl nitrite was 4.4×10^{-11} moles per chart paper area unit per microliter of nitromethane injected into the chromatograph with the attenuation factor of the instrument set at unity. For Run No. 44 and a dose of 21.6×10^{21} e.v. the number of area units was 0.60 per microliter of solution with the instrument on an attenuation of 40. The moles of methyl nitrite were

TABLE 2

Mole Fractions of Minor Radiolysis Gaseous Products from Runs at Room Temperature

Run no.	Temperature °C	Gamma ray dose electron volts $\times 10^{-22}$ per mole of CH_3NO_2	Mole fraction of products $\times 10^5$							
			N_2	NO	N_2O	CO	CO_2	H_2	CH_4	C_2H_6
4	26	2.11	11.5	18.7	6.5	5.8	10.4	5.8	3.5	1.7
7	26	2.09	10.7	16.4	6.6	6.8	8.4	6.2	3.9	2.8
8	27	1.40	7.6	6.8	2.6	3.2	4.1	3.0	0.9	1.6
9	28	1.40	6.3	8.4	3.2	4.4	3.5	3.7	1.6	1.8
10	28	0.70	2.5	--	--	1.7	--	1.6	0.6	--
11	28	0.70	2.5	2.9	0.7	2.2	3.0	1.6	0.7	0.5
12	28	0.70	--	2.6	0.7	--	1.5	--	--	0.6
13	27	0.35	0.8	1.2	0.2	0.6	1.6	0.9	0.5	0.3
19	27	0.34	1.2	0.8	0.2	0.5	1.2	0.7	0.5	0.3

TABLE 3

Mole Fractions of Minor Radiolysis Gaseous Products from Runs at 0°C

Run number	Gamma ray dose electron volts x 10 ⁻²² per mole	Mole fraction of products x 10 ⁵							
		N ₂	NO	N ₂ O	CO	CO ₂	H ₂	CH ₄	C ₂ H ₆
15	0.70	2.2	2.4	0.3	1.3	0.7	2.0	0.7	0.4
16	0.70	2.6	1.2	0.4	1.4	1.2	2.1	0.7	0.7
17	0.70	2.3	2.2	0.3	1.5	0.5	2.1	0.9	0.2
18	1.28	4.6	--	--	3.8	--	3.8	1.4	--
19	1.28	5.0	2.7	0.7	3.9	1.1	3.7	1.3	0.8
20	1.28	4.6	3.2	0.7	3.8	1.1	3.8	1.5	0.7
21	1.89	6.7	4.5	1.1	6.4	1.7	5.5	2.5	1.1
23	1.88	6.4	5.5	1.5	6.4	3.0	5.2	2.2	0.9
24	0.32	--	2.5	0.4	--	0.21	--	--	0.4
30	0.31	0.6	1.4	0.2	0.2	1.2	0.41	1.0	0.1
31	0.31	0.8	1.4	0.2	0.2	0.6	1.1	0.6	0.1
32	0.62	--	2.0	0.6	--	1.6	--	--	0.4

$$4.4 \times 10^{-11} \times 0.60 \times 40 = 1.05 \times 10^{-8} \text{ moles}$$

But, this represents the moles of methyl nitrite in one microliter of nitromethane. In five milliliters (0.0926 moles at 25°) there were 52.7×10^{-6} moles and the mole fraction was 57×10^{-5} . Formaldehyde and methyl nitrate were similarly analyzed. The results are given in Table 4.

Residue analysis

An infrared spectrum of the water soluble residue from a 2 hour run at 0°C is shown in Figure 9, along with the spectrum for pure cis-nitrosomethane dimer. Figure 10 shows the ultraviolet spectrum of the water solutions of residue and pure dimer.

Figure 11 shows the infrared spectrum of the water insoluble fraction and the spectrum for formaldoxime trimer prepared according to the method of Taylor and Bender.⁴⁰

These figures indicate that the residue, in addition to containing the nitroso dimer and formaldoxime (and probably a trace of nitromethane not removed by vacuum distillation), also contains other radiolysis products. These were not definitely identified. Compounds containing the carbonyl group as well as oxygen-nitrogen bonds may be present.⁴¹ Formaldehyde or any of its polymers was not identified.

In spite of possible interference from these additional compounds,

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

(41) W. West, ed., "Chemical Applications of Spectroscopy," Interscience Publishers, Inc., New York, N. Y., 1956, pp. 443-59; 537-45; 563-80. This book is Vol. IX, in the series, "Technique of Organic Chemistry," A. Weissberger, ed.

TABLE 4

Production of Formaldehyde, Methyl Nitrite, and Methyl Nitrate

- 25° -					- 0° -				
Run no.	Dosage e.v./mole $\times 10^{-21}$	Average mole fraction $\times 10^5$			Run no.	Dosage e.v./mole $\times 10^{-21}$	Average mole fraction $\times 10^5$		
		CH ₂ O	CH ₃ ONO	CH ₃ ONO ₂			CH ₂ O	CH ₃ ONO	CH ₃ ONO ₂
40	11.7	--	--	1.8	39	20.0	00	00	3.8
41	6.7	--	--	0.7	42	10.7	--	--	1.5
44	3.0	14.0	9.7	0.9	45	3.3	8.7	5.2	0.6
44	8.7	25.9	17.3	1.4	45	9.8	10.6	7.8	1.5
44	14.8	52.3	26.6	2.5	45	14.2	19.6	13.0	2.1
44	17.6	61.5	57.2	--	46	17.8	--	24.2	3.0
47	21.8	--	--	4.6					
48*	15.8	--	34.0	2.1					
51	5.5	--	9.8	--					
51	11.0	--	21.0	--					
51	13.7	--	25.0	--					

* Methyl nitrite was determined optically in this run

A. Water soluble residue from a run at 0°C., paste smeared on NaCl cell window. B. cis-Nitrososome dimer, KBr disc.

Figure 9.-- Comparison of the Infrared spectra, Part I.

A-Spectrum of the water soluble residue from a typical run.

B-Spectrum of cis-Nitrosomethane dimer.

Figure 10.--Comparison of Ultraviolet spectra.

A - Water insoluble residue from a run at 0°, KBr disk
B - Formaldoxime trimer

Figure 11.— Comparison of Infrared spectra, Part II.

it was assumed that only the cis dimer contributed to the optical absorption at 265 mμ. Thus, when the residue from Run No. 35 was dissolved in 250 ml. of water the absorbance was 0.690. The extinction coefficient is 1×10^4 liters per mole cm.

The concentration of cis dimer was

$$0.690 \text{ cm}^{-1} / 1.0 \times 10^4 \text{ liters mole}^{-1} \text{cm}^{-1} = 6.9 \times 10^{-5} \text{ mole/liter}$$

In 250 ml there were 1.72×10^{-5} moles. Therefore, the mole fraction of dimer was 18.6×10^{-5} . The results for other doses are shown in Table 5.

Unlike the cis isomer the trans nitrosomethane dimer is volatile. Had any trans dimer been formed during an irradiation, it might have vacuum distilled during the nitromethane removal. To check this possibility and also the stability of the cis isomer in nitromethane, a small amount of the latter isomer was dissolved in degassed nitromethane and allowed to stand in the dark at 25°C for a week. Then, the nitromethane was vacuum distilled. The residue was dissolved in water. The ultraviolet spectrum showed a shift toward longer wavelengths, with the maximum at 270 mμ. This is an indication that some of the cis isomer was converted to the trans, which has a maximum at 276 mμ. It also shows that although the trans isomer is volatile, enough was retained to give evidence of its presence in the residue.

The distilled nitromethane was then examined for dissolved trans isomer. One milliliter of the nitromethane was treated with chromatopic acid according to the method of Bricker and Vail.⁴²

(42) C. E. Bricker and W. A. Vail, Anal. Chem., **22**, 720 (1950).

TABLE 5

Production of Cis Nitrosomethane Dimer at 0° and 25°

Run no.	Dose e.v. x 10 ⁻²¹ - 25° -	Mole fraction x 10 ⁵	Run no.	Dose e.v. x 10 ⁻²¹ - 0° -	Mole fraction x 10 ⁵
These runs were not numbered	3.5 1.7 0.9 10.5 19.5	3.3 1.6 0.9 13.5 11.4	18 13 23 29 26	14.1 14.0 20.7 3.5 0.9	14.1 12.9 22.7 3.2 0.3
36 37 39 41	19.5 12.9 6.5 15.8	7.7 13.8 7.1 12.5	27 28 29 30 32 33 35 42	0.9 1.7 6.9 3.4 6.9 13.6 20.4 10.6	0.3 1.4 6.0 3.0 5.8 13.5 18.6 10.2

In this method a solution of formaldehyde in an organic liquid is heated to dryness in the presence of chromatropic acid. Sulfuric acid is then added and after heating, a purple coloration results which can be measured quantitatively on a spectrophotometer. Formaldoxime also gives a positive test. Thus, heating a solution of trans nitroso dimer would convert some of it to the monomer which would isomerize to formaldoxime to give a positive test with chromatropic acid. However, the test was negative, leading to the conclusion that, if trans dimers were a radiolysis product, it would still be retained in the residue when the nitromethane was vacuum distilled at 0°C. The formation of the cis rather than trans isomer under the influence of radiation is in agreement with the findings of others.^{35,37}

Dark reaction

The data listed in Tables 2, 3, 4, and 5 were plotted to give Figures 12-23. These results show that for many of the products the concentrations are not linear with dose. Interestingly enough, the products which show this nonlinearity are also produced in the dark reaction; that is, they are produced even after removal from the gamma ray source. These products are methyl nitrite, methyl nitrate, N_2 , N_2O , CO_2 , and CH_4 . Formaldoxime, although not shown in any figure is also a product of the dark reaction.

Additives

Several experiments were done in which NO_2 or water was added before irradiation. Nitrogen dioxide interferes with gas chromatographic determinations so only qualitative results were obtained.

Figure 12. Formaldehyde production at 0° and 25°C.

Figure 13.--Cis-Nitrosomethane dimer production at 0° and 25°

Figure 14.--Production of Methyl nitrite at 0° and 25°

Figure 15. Carbon monoxide production at 0° and 25° C.

Figure 16.--Hydrogen production at 0° and 25°C.

Figure 17.--Nitric oxide production at 0° and 25°C.

Figure 18.---Nitrogen production at 0° and 25° C.

Figure 19.-Methyl nitrate production at 0° and 25°C.

Figure 20.--Carbon dioxide production at 0° and 25°C.

Figure 21.-Nitrous oxide production at 0° and 25°C.

Figure 22.--Ethane production at 0° and 25° C.

Figure 23.--Methane production at 0° and 25° C.

Upon irradiation the yellow solution of NO_2 in nitromethane became blue-green, and when frozen at -196°C , the solid showed a strong blue color indicative of N_2O_3 . In spite of NO_2 interference gas chromatographic analysis showed that methyl nitrite concentration was much reduced, although the yield of nitrate was not affected. There was no residue and hence the nitrosomethane dimer was absent. Tests with chromatropic acid showed that the mole fraction of formaldehyde and/or formaldoxime was about 10^{-3} for a 3 hour run at 25° . This was ten times the yield in the absence of dissolved NO_2 .

When water was added to make a nearly saturated solution in nitromethane at 25° , the result was an additional peak at $384 \text{ m}\mu$ on the spectrophotometer. As the irradiation continued this peak changed to the shoulder typical of methyl nitrite as shown in Figure 24. Gas chromatographic analysis for methyl nitrite gave the results shown in Figure 25. These results show that the methyl nitrite yield was initially reduced.

G-values

Once the mole fraction of product was known as a function of dose, it was possible to calculate the G-values. G-value is the number of molecules formed or decomposed per 100 electron volts of energy absorbed. To obtain the G-value at a given absorbed dose, the slope of mole fraction versus dose per mole was multiplied by Avogadro's Number times 100. This is most easily done when the dose dependence is linear. For nonlinear dependence a tangent was drawn to the line to give the instantaneous G-value at that dosage.

Figure 24.--Change in the relative peaks heights at 3750 Å and 3830 Å with gamma ray dose for a solution of water in Nitro-methane at 25°C.

Figure 25.—Methyl nitrite production at 25° in Nitromethane containing water.

As an example of the former situation the slope for formaldehyde at 25° is 3.46×10^{-26} moles/electron volt.

$$G(\text{CH}_2\text{O}) = (3.46 \times 10^{-26})(6.02 \times 10^{23})(10^2) = 2.0$$

For methyl nitrite at a dose of 10^{22} e.v. the G-value is $(1.84 \times 10^{-26})(6.02 \times 10^{23})(10^2) = 1.11$. However, when the total dose is increased to 1.6×10^{22} , $G(\text{CH}_3\text{ONO})$ is 7.4.

G-values are listed in Tables 6 and 7. The values in these tables were then used to construct Figures 26-28.

Mass balance

Table 8 shows the results for mass balance analyses for several doses at 0° and 25°C. Allowing for experimental errors, the ratios are nearly constant over the absorbed dose range studied. Ideally the mole ratios of H/C, N/C, and O/C should be 3/1, 1/1, and 2/1 respectively. The actual ratios fall short of the ideal, especially for oxygen. The nitrogen and hydrogen ratios approach more nearly to the theoretical at 0° than 25°C. The oxygen ratio is independent of temperature.

Deviations from the theoretical values were to be expected, because formaldoxime and water were not quantitatively analyzed, although identified as products. These two products alone do not satisfy the problem, however. For instance the nitrogen to carbon ratio in formaldoxime is only one to one, whereas it should be higher if the theoretical ratio is to be achieved for the overall mass balance. To see this more clearly, consider the following equations,

TABLE 6
Instantaneous G-Values at 25°C for Various Doses

Dose (e.v./mole x 10 ⁻²¹)	0	5	8	10	12.5	15	18	20
(CH ₃ NO) ₂	0.53	0.70	1.3	0.47	0.0	-0.25	--	-1.0
CH ₂ O	2.0 for all doses							
CH ₃ ONO	1.1	1.1		1.1		3.1	7.4	--
CH ₃ ONO ^a	0.37	0.51		0.94	1.35 ^b	2.1 ^c		
NO	0.09	0.32		0.45		0.73		2.7
CO ₂	0.16	0.16		0.16		0.24	0.55	0.87
CO	0.18 for all doses							
H ₂	0.17 for all doses							
N ₂	0.20	0.24		0.30		0.40		0.42
N ₂ O	0.02	0.08		0.16		0.27		0.37
CH ₃ ONO ₂	0.09	0.09		0.09		0.09	0.15	0.32
C ₂ H ₆	0.06 for all doses							
CH ₄	0.07	0.07		0.07		0.07	0.21	0.26

^a from nitromethane containing water.

^b at a dose of 12.0 x 10²¹ e.v.

^c at a dose of 14.0 x 10²¹ e.v.

TABLE 7
Instantaneous G-Values at 0°C for Various Doses

Dose (e.v./mole x 10 ⁻²¹)	0	5	10	15	18	20
(CH ₃ NO) ₂	0.53	0.54	0.68	0.73		0.81
CH ₂ O	0.84 for all doses					
CH ₃ ONO	0.60	0.60	0.60	1.2	2.9	
NO	0.009 for all doses					
CO ₂	0.07 for all doses					
CO	0.18 for all doses					
H ₂	0.17 for all doses					
N ₂	0.20 for all doses					
H ₂ O	0.02		0.04			0.06
CH ₃ ONO ₂	0.09	0.09	0.09	0.09	0.15	0.32
C ₂ H ₆	0.03 for all doses					
CH ₄	0.07	0.07	0.07	0.07	0.12	0.26

Figure 26-Dose dependence of G-values of major products at 25°.

Figure 27.-Dose dependence of G-values of minor products at 25°.

Figure 28.--Nonlinear dose dependence for G-values at 0° C.

TABLE 8
Elemental Mole Fractions for Various Doses

Element*	Temperature °C	Dose x 10 ⁻²¹				
		5	10	12	15	18
Carbon	25	39.7*	84.6	98.1	112.5	156.2
	0	21.1	44.2	53.7	68.8	92.3
Nitrogen	25	24.9	59.5	68.7	74.4	121.0
	0	17.5	37.2	45.0	59.6	83.0
Hydrogen	25	98.2	212.2	245.8	274.8	391.5
	0	55.5	117.2	143.3	183.6	249.9
Oxygen	25	52.5	109.3	129.5	151.7	235.1
	0	27.5	57.6	70.9	90.0	126.3

* Mole fractions are times 10⁵

$$\left(\frac{N}{C}\right)_{\text{ideal}} = \frac{1}{1} = \frac{\sum_{i=1}^{n_N} a_i N_i}{\sum_{i=1}^{n_C} b_i C_i} \quad \text{I}$$

where N_i and C_i are the mole fractions of each product containing nitrogen and carbon, respectively. Each mole fraction must be multiplied by the number of atoms of nitrogen or carbon appearing in the molecule, hence a_i and b_i . For the actual system, though, we have

$$\left(\frac{N}{C}\right)_{\text{actual}, 25^\circ} = 0.7. \quad \text{II}$$

If the assumption is made that the difference is entirely due to formaldoxime this ratio will approach more closely to one, but cannot attain that value, so that the assumption is false.

Moreover, the addition of formaldoxime, CH_2NOH , will cause the O/C ratio to become even smaller, since its ratio in formaldoxime is only 1/1.

What about water? The presence of water would account for some of the missing oxygen, but a limitation is imposed by the H/C ratio. Thus, we have

$$\left(\frac{H}{C}\right)_{\text{actual}, 25^\circ} = 2.5 = \frac{\sum_{i=1}^{n_H} d_i H_i - 2[\text{H}_2\text{O}]}{\sum_{i=1}^{n_C} b_i C_i} \quad \text{III}$$

but the theoretical value is 3/1 or,

$$\left(\frac{H}{C}\right)_{\text{ideal}} = \frac{3}{1} = \frac{\sum_{i=1}^{n_H} d_i H_i}{\sum_{i=1}^{n_C} b_i C_i} \quad \text{IV}$$

where C_1 , H_1 , d_1 , and b_1 have the same meaning as before, except that H_1 and b_1 refer to hydrogen. Substituting in equation III gives

$$2.5 = \frac{\sum_{i=1}^{n_H} d_i H_i - 2[H_2O]}{\sum_{i=1}^{n_H} d_i H_i / 3} \quad V$$

The ratio of $\sum_{i=1}^{n_H} d_i H_i / [H_2O] = 12/1$. Next, this ratio may be

applied to the results given in Table 9. For instance at 25°C , and a dose of 12×10^{21} e.v., $\sum_{i=1}^{n_H} d_i H_i - 2[H_2O]$ is 245.8×10^{-5} mole fraction.

Then, we have

$$\begin{aligned} 12[H_2O] - 2[H_2O] &= 245.8 \times 10^{-5} \\ [H_2O] &= 24.6 \times 10^{-5} \end{aligned}$$

If this value is added to that for oxygen at this dose, we have $(24.6 + 129.5) \times 10^{-5}$ or 155.1×10^{-5} mole fraction. The O/C ratio will then be 1.58 which is still not enough to account for all the oxygen.

If the formaldoxime and water are considered together, the results will be even worse in terms of oxygen balance because the ratio of hydrogen to carbon in formaldoxime is the theoretical 3 to 1.

The presence of one or more other products in addition to water and formaldoxime has been shown by the infrared and ultraviolet spectra pictured in Figures 9, 10, and 11. It has been mentioned previously that interference from these unknown products could cause

TABLE 9
Ratios of the Elements at Various Doses

Ratio	Temperature °C	Dose $\times 10^{-21}$				
		5	10	12	15	18
H/C	25	2.47	2.51	2.51	2.44	2.51
	0	2.63	2.65	2.67	2.67	2.71
N/C	25	0.63	0.70	0.70	0.71	0.77
	0	0.83	0.84	0.84	0.87	0.90
O/C	25	1.32	1.29	1.32	1.35	1.55
	0	1.30	1.30	1.32	1.31	1.37
H/N	25	3.94	3.57	3.58	3.46	3.26
	0	3.17	3.15	3.18	3.08	3.01
H/O	25	1.87	1.94	1.90	1.81	1.62
	0	2.02	2.03	2.02	2.04	1.98
O/N	25	2.11	1.84	1.89	1.91	2.01
	0	1.57	1.55	1.58	1.51	1.52

errors in the quantitative analysis of nitrosomethane, and hence, in the mass balance. Even if there were no interference, simply the omission of this product (or products) would cause errors in the mass balance.

Although it is difficult to say what compounds might have been missed in the analysis, the mass balance ratios permit certain observations. First of all carbon is in excess. This would reduce the probability that compounds containing two or more carbon atoms are present. Conversely, the chances for compounds containing no carbon at all would be increased.

The possibility of the presence of undetected inorganic compounds is further increased by the methods of analysis, which depend heavily on gas chromatography and infrared spectroscopy for qualitative and quantitative detection. Infrared detection, because of the small conversions involved in this work is rather limited to products that can be concentrated in the gas phase. This same limitation applies also to gas chromatography employing thermal conductivity detection. On the other hand, flame ionization detection although extremely sensitive to most organic compounds, is much less useful for the detection of inorganic compounds which might be present.

CHAPTER IV

DISCUSSION

Introduction

The next step is to consider the various radiolysis products and how they originate. No product, not even nitrosomethane, has been observed in this study that has not been observed before, either by pyrolysis or photolysis or both. Consequently, at least some of the mechanisms proposed previously to account for products may also apply here. Generally speaking the difficulty will not be in finding a mechanism to account for a product, but in deciding which of several possible mechanisms is the best choice. Indeed it may be found that a product does arise by more than one means.

When nitromethane, or any other substance for that matter, is irradiated with gamma rays, it is generally accepted that the first event of chemical importance will be ionization.

Here $\rightsquigarrow$ indicates the presence of ionizing radiation.

It might also be well to point out that by introducing ionization a number of possible reactions enter the picture which have not been considered previously. Heretofore, all work with the exception of mass spectrometry has been confined to thermal excitation or light of energy not sufficient to cause ionization. The conditions

of the present study of the liquid, however, are far removed from those that occur in the mass spectrometer where we are dealing with gases at very low pressures.

Following ionization of the nitromethane several alternatives are possible which are not necessarily mutually exclusive. There may be recapture of the electron to form an excited molecule which by collision can be deactivated.

where * indicates an excited molecule, and M is any other molecule that can dissipate the excess energy. Since this situation does not lead to products, however, it will not be considered further.

A second possibility is the dissociation of the excited molecules into free radicals. As shown in the Historical Review, the reactions that have been postulated as the source of the original free radicals are

Next there is the possibility of the dissociation of the ionized parent molecule into daughter ions and free radicals as observed in a study of the positive ion spectrum by Kandel.

A minor reaction in the mass spectrometer of interest is

In this last reaction the appearance potential of nitrosomethane or formaldoxime is the same as the ionization potential of nitromethane (11.3 e.v.).

Finally, there are negative ions to consider as shown by the work of Henglein and Muccini.²³ These negative ions could be formed when a neutral nitromethane molecule captures an electron released in (1).

Furthermore, it has been shown that the capture process can occur without activation. Thus, solvated electrons and reactions dependent on solvated electrons are unlikely, but may be significant.

Which of the above reactions takes place will depend on several factors. One of these is the stability of CH_3NO_2^+ in solution. It appears that this ion is fairly stable in the mass spectrometer, since it is 53.5% as abundant as the most prevalent ion. This is important because it may allow the ion to exist long enough to recapture the electron [equation (2)] and then decompose by (5), (6), or (7). Chances are good that CH_3NO_2^+ is collisionally stabilized in the liquid phase.

Another factor of importance is the dielectric relaxation time, i.e., the time required for short range order to be re-established in the liquid following the disturbance caused by the ionization process in the medium. Thus an electron which is ejected during the ionization process may escape recapture by being shielded from the positive ion by intervening molecules if the dielectric is quickly restored. In nitromethane where it has been shown that electron capture by neutral molecules is an important process, recapture by the positive ion is even less likely to occur.

Cage effects must also be considered. Nitromethane is a highly polar liquid and it is likely that hydrogen bonding is present to increase the chances of cage effects.

Suppose that the electron does escape recapture. What happens, then to CH_3NO_2^+ ? If it has a long lifetime, it must eventually neutralize one of the negative species formed in reactions (11), (12), and (13). The negative ion CH_2NO_2^- is stable in nitromethane and is the anion formed when nitromethane is dissolved in an aqueous basic solution. Therefore, the neutralization reaction is most apt to be

Here "products" may be radicals as well as molecules.

The ion, CH_3NO_2^+ may decompose into daughter ions and radicals before neutralization occurs, as in equations (8), (9), and (10).

Equation (8) is of special interest, because there is some uncertainty as to whether it or reaction (15) following (9) is responsible for NO. Kandel²² favors (8) because of bond energy requirements. Reaction (8)

on the other hand requires rearrangement of the CH_3NO_2 molecule during ionization and dissociation which is a mechanism that has fallen out of favor recently, at least in photolytic work.

Reaction (10) is of interest because its appearance potential is the same as the ionization potential of nitromethane, and so it would seem that less energy is required to produce CH_3NO^+ (or CH_2NOH^+) than the other ions. Hence, it might be expected that this is a significant step in the decomposition. But, in the mass spectrometer CH_3NO^+ is a minor product, 8.5 times less common than CH_3NO_2^+ and 16 times less than NO^+ . Moreover, in the mass spectrometer the ion appears to be CH_2NOH^+ , formed by an exothermic rearrangement of CH_3NO^+ .

Reactions (10) and (12) do emphasize an important difference between radiation induced reactions and thermal reactions and to a lesser extent photochemical reactions - the weakest bond is not always the first to be broken.

With these considerations as background, the products and possible mechanisms for their origins may be discussed.

Formaldehyde

I begin with formaldehyde for two reasons. Initially, it has the largest G-value at 25° (2.0). Secondly, unlike most of the other products, $G(\text{CH}_2\text{O})$ remains constant over the dose range studied. On the other hand there is a temperature effect, $G(\text{CH}_2\text{O})$ being only 0.84 at 0°. Although it is dangerous to generalize from only two

temperatures, this difference gives an overall apparent activation energy of about 6 kcal/mole for CH_2O formation.

It is difficult to say which, if any, of the mechanisms suggested for the formation of CH_2O actually occur. Hirschlauff and Norrish¹ proposed an intramolecular rearrangement,

It has also been suggested that formaldehyde arises from the reaction of NO_2 with the radical, CH_2NO_2 ,⁶ the implied mechanism being,

There are also several other ways that may lead to CH_2O . Should methyl and methoxyl radicals be present resulting from equations (5) and (8), there may be

Since formaldoxime and water are known products, the hydrolysis may occur.

Going farther afield aldehydes are also formed when a salt of a nitroparaffin reacts with an alkyl halide.⁴³ This reaction involving nitromethane can be written as

(43) N. Kornblum, P. Pink, K. V. Yorka, J. Am. Chem. Soc., **83**, 2779 (1961).

where X is a halide and R is some organic group such as methyl, phenyl, etc.

In the present study a neutralization reaction such as (14) might give similar products.

When discussing these possible reactions it might be better to put (7) as,

More could be said about (7) if the fate of the HNO radical were known. It has been postulated that in the gas phase, reactions (22) or (23) occur.^{1,44}

In the liquid these reactions might not occur. Neither N_2O , nor N_2 are major products, $G(\text{N}_2)$ initially being 0.20, and $G(\text{N}_2\text{O})$, 0.02, at 25° .

Reaction (17) is a disproportionation reaction of methoxyl radicals and requires no activation.⁴⁵ The same is true for (18).⁴⁵ Furthermore, methane was a very minor product and methanol was scarcely above detectable limits. On the other hand methanol reacts readily with NO_2 , (N_2O_4) to give the nitrite.³⁰

(44) J. B. Levy, *ibid.*, 78, 1780 (1956).

(45) P. Gray and A. Williams, *Chem. Rev.*, 59, 239 (1959).

This may account for the absence of methanol.

There does not appear to be any information available on the ease of hydrolysis for formaldoxime. The monomer is slightly soluble in cold water and decomposes in hot water. Reaction (19) presumably is an ordinary bimolecular reaction and so would probably have a much greater activation energy than the observed 6 kcal.

Neither can much be said about (21). The Arrhenius activation energy for the similar reaction,

in

in aqueous solution at 25° is 15.2 kcal/mole.⁴⁶
Reaction (16) is of some interest, especially since it was

shown experimentally that the addition of NO₂ to nitromethane leads to an apparent G(CH₂O) of 20, and also to the formation of a large amount of NO which was not quantitatively determined. This apparent G(CH₂O) must be treated cautiously, because the method of analysis did not distinguish between CH₂O and CH₂NOH. Nevertheless, a G-value this large suggests that a chain mechanism is involved when NO₂ is initially present.

Chain mechanisms have been suggested before.^{8,10} That of Hillenbrand and Kilpatrick⁸ may apply here. As will be recalled from the Historical Section of Chapter I, for the thermal decomposition this was,

(46) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 1st ed., John Wiley and Sons, Inc., New York, N. Y., 1953, p. 131.

Experimentally, it was observed in the present study that NO_2 does not react with CH_3NO_2 at room temperature so that at first it would seem unlikely that reaction (26) would occur.

Kandel¹⁸ has discussed the ionization potential of NO_2 and has found that it may be as low as 9.9 volts. This is much less than that of CH_3NO_2 which is 11.3 volts. When a solution of NO_2 in nitromethane is irradiated, a charge transfer may take place.

Thus, although a thermal reaction (26) does not occur, reactions of an ionized or excited NO_2 molecule with CH_3NO_2 leading to CH_2O formation may be possible instead.

The discovery of 1,2-dinitroethane, resulting from radical recombination, would have been good support for the existence of the CH_2NO_2 radical, according to the equation (29).

Gas chromatograms of the irradiated nitromethane did show traces of high boiling materials. Unfortunately, these could not be positively identified.

Hydrogen and carbon monoxide

Hydrogen and carbon monoxide, although minor products, have, like formaldehyde, G-values that remain constant as the absorbed dose increases. Unlike formaldehyde, however, $G(\text{CO})$ and $G(\text{H}_2)$ are also independent of temperature at least at 0° and 25°C . Furthermore, $G(\text{CO})$ and $G(\text{H}_2)$ have very nearly the same value, 0.18.

These findings may be contrasted to thermal decomposition where hydrogen does not appear to have been observed at all and to photolysis where hydrogen production is about a third of that of CO .^{17,18}

The similar behavior of CO and H_2 suggests that both are formed in the same step or same sequence of steps. Moreover, the uniqueness of their behavior also suggests that H_2 and CO are formed in a way unique to radiolysis such as a neutralization step. Thus, instead of (21), there may occur,

Should neutralization be the source of CO and H_2 , it is interesting to note that the small values of $G(\text{H}_2)$ and $G(\text{CO})$ compared to some of the other products may indicate that the usual fate of the electron is to avoid recapture by the parent ion. This would be in keeping with the ease of negative ion formation as shown by Henglein and Muccini.²³

Nitric oxide, nitrogen dioxide, and nitrous acid

Nitric oxide was initially a very minor product, nitrogen dioxide was not observed, and the evidence for nitrous acid was

only indirect. Yet, these species probably play an important part in the decomposition of nitromethane.

The first two compounds listed above are in a sense stable free radicals, since each contains an unpaired electron. Hence it is not surprising that they should be quite reactive in a system in which transient free radicals are created. Nitrogen dioxide must be particularly reactive, because it has seldom been observed in any CH_3NO_2 kinetic study. Furthermore, NO, because of its low boiling point would be more likely to escape from the nitromethane and so escape other reactions.

Figures 17 and 26 show how NO concentration and G-value vary with gamma ray dose. At 0° $G(\text{NO})$ remains small and constant over the entire dose range studied. At 25° after an initial G-value of 0.09, the same as at 0° , it slowly increases, becoming 2.9 at 2.0×10^{22} e.v. This nonlinear behavior is not surprising when the complicated reactions that NO may undergo are considered. Possible sources of NO are reactions (8), (15), and (16).

Nitric oxide may react with methyl radicals to form nitrosomethane although it seems more probable that in the present system nitrosomethane is formed by (12), because of the ease of electron capture. No matter how it is formed, CH_3NO reacts in a complicated manner with NO. This reaction has been studied by several investigators and will be discussed in more detail in the section dealing with nitrosomethane reactions.

Nitrogen dioxide produced by (5) or (8) and which does not dissociate into NO and O may react as in (16), or possibly as an excited or ionized species with nitromethane.

It may also recombine with methyl radicals to reform the parent molecule or to produce methyl nitrite.¹⁸

Note that (3) and (31) are chain terminating steps for the reactions leading to formaldehyde formation. Thus, when NO_2 is not in excess as when it was dissolved in nitromethane, the rate of reaction of CH_3 and NO_2 may be sufficiently great to prevent a chain mechanism. In this connection, it should also be noted, that when NO_2 was dissolved in CH_3NO_2 , methyl nitrite formation was reduced below that formed in the absence of added NO_2 .

There is no direct evidence for the presence of nitrous acid. The compound is too unstable to be observed in the gas phase, and instead exists as an equilibrium mixture as shown in equation (27). It has, however, been extensively studied in solution⁴⁷ and its ultraviolet spectrum obtained by several workers.⁴⁸⁻⁹ As might be expected from the similarity of structure the spectrum is much the same as methyl nitrite. In the wavelength range permitted by liquid nitromethane ($> 370 \text{ m}\mu$) HONO and CH_3ONO solutions may be distinguished

(47) For a review of HONO and some of the chemical species associated with it, see J. A. Turney and G. A. Wright, Chem. Rev., **59**, 497 (1959).

(48) N. S. Bayless and D. W. Watts, Australian J. Chem., **9**, 319 (1956).

(49) H. Singer and P. A. Vamplew, J. Chem. Soc., **1956**, 3971.

by the fact that HONO shows an absorbance peak at 384 μ whereas methyl nitrite has only a shoulder at that wavelength.

When a solution of water in nitromethane was irradiated the spectrum shown in Figure 24 was obtained. The spectrum shows just such a peak at 384 μ . As the irradiation continues this peak is converted to a shoulder, which as Figure 25 shows, is consistent with the growth of methyl nitrite. Irradiated nitromethane which does not contain water added before irradiation also shows this peak at 384 μ , but for a much shorter radiolysis time. Unfortunately, this is not absolute proof for the presence of nitrous acid, because there may be other compounds present that also have a peak at 384 μ .

More circumstantial evidence favoring the presence of HONO is provided by the mass balance ratio discussed above. It was shown that the amount of carbon found when compared to the other elements was in excess of the stoichiometry required by the formula, CH_3NO_2 . In other words, there was a deficiency of H, N, and O. Hence, this deficiency may be explained by the presence of undetected HNO_2 , (and water).

If nitrous acid were present, several questions would be raised. First, why does water increase the concentration of HNO_2 ? There are several possible answers to this question. Nitrous acid may result from the hydrolysis of methyl nitrite.

This agrees with the initially reduced G-value for methyl nitrite, but gas chromatographic analysis revealed no increase in methanol concentration.

Another explanation depends on equation (27) which shows that HONO is in equilibrium with H_2O , NO, and NO_2 . The addition of water would drive the equilibrium toward the formation of more HONO. This would probably also reduce the concentration of NO_2 available to form CH_3ONO .

Secondly, why does HONO disappear as the dose increases? Again, there are several possible answers. Nitrous acid disproportionates to form nitric acid.⁵⁰

Nitrous acid may react with nitromethane to form methyl nitrolic acid.⁵¹

Finally, because it is in equilibrium with NO_2 and NO, the reactions of these species would reduce the HONO concentration to some low steady state value.

However, the questions of why the observed mass ratios of N/C and H/C approach more closely to the theoretical value at 0° than at 25° and why O/C remains unchanged is unresolved.

Nitrosomethane

When discussing nitrosomethane, one must remember that the compound was not observed as a monomer, but rather as a dimer. This

(50) E. de B. Barnett and C. L. Wilson, "Inorganic Chemistry, A Textbook for Advanced Students," Longmans Green and Co., London, England, 1953, p. 351.

(51) N. V. Sidgwick, "The Organic Chemistry of Nitrogen," Oxford Press, Oxford, England, 1937, p. 241.

distinction is necessary because we are dealing with events in solution where both species occur. Only after the nitromethane was removed, was the cis dimer obtained.

Moreover, when two geometrical isomers were possible only the cis was found. Yet as mentioned previously, when the pure cis dimer was dissolved in nitromethane, it was partially converted to the trans isomer. Why is only the cis isomer found in the irradiated solution?

Here again, the influences of solvent and radiation were important. A diagram shown below and taken from the work of Gowenlock and Trotman³⁵ shows the relationship of monomer and dimers.

Nitromethane has an intermediate dielectric constant when compared to water, and say, carbon tetrachloride. At 0° it is 45 and at 20°, 39.⁵² When the cis dimer was dissolved in ethanol at 25°, the cis form was converted into the trans isomer within 36 hours.³⁵ Ethanol has a dielectric constant of 26.5 at 20°.⁵² In nitromethane with its higher dielectric constant the transformation was only partly complete

(52) "International Critical Tables," McGraw-Hill Book Co., New York, N. Y., 1929, Vol. 6. pp. 83, 101.

in a week at 25⁰. Thus, as the diagram above shows the combination of moderately high dielectric constant plus radiation would tend to favor the cis isomer.

The diagram also shows that water favors the conversion of the monomer to formaldoxime instead of to dimer, and that even in non-aqueous solvents continued irradiation also leads to formaldoxime. Thus in nitromethane with its fairly high dielectric constant the conversion of nitrosomethane monomer to formaldoxime may be an important competing reaction to dimer formation.

Interestingly, and in agreement with the present work, when the dimer is prepared by the decomposition of acetyl peroxide in a liquid alkyl nitrite at elevated temperature (Karasch, Meltzer, Nudenberg synthesis⁵³), the cis dimer is formed rather than the trans.³⁷ This result is in contrast to the results of the original KMN synthesis which led to the formation of the trans isomer. However, in the latter work, the product of the synthesis was purified by recrystallization from carbon tetrachloride. As has been shown, any cis isomer present would be converted to the trans isomer by this solvent.³⁵

Figure 13, 26, and 28 show the relationship of concentrations and G-values to absorbed gamma ray dose at 0⁰ and 25⁰ for the cis dimer. These figures reveal that initially $G(\text{CH}_3\text{NO})_2$ is the same at 0⁰ and 25⁰, but as the dose increases the G-values diverge greatly. This divergence is probably due to the secondary reactions that the nitrosomethane monomer may undergo, these reactions being more prominent at 25⁰.

(53) M. S. Karasch, T. H. Meltzer, and W. Nudenberg, J. Org. Chem., 22, 37 (1957).

When mechanisms for the formation of the monomeric nitroso-methane are considered, there are as usual several possibilities.

None of the above can absolutely be ruled out, although reactions (12) and (36) are likely to be the most important. Reaction (36) has the great advantage of having been observed in the gas phase.^{2,54} Moreover, the presence of NO among the products and of small amounts of CH_4 and C_2H_6 , indicative of methyl radicals, favors (36). At the same time reaction (12) should also be important. As stated earlier, electron capture in CH_3NO_2 has been shown to occur with no energy barrier, so that in the radiolytic system with its secondary electrons, electron capture should readily occur. Hence the sequence of reactions (11), (12), and (13) which have been observed in the mass spectrometer should also be important in the radiolytic system.

Secondary reactions of nitrosomethane

Nitrosomethane monomer is a reactive species and can participate in a number of reactions that have been studied.

(54) M. I. Christie, J. S. Frost, and M. A. Voisey, Trans. Faraday Soc., **61**, 674 (1965).

Among these reactions is methyl radical addition.⁵⁵

Probably more important in the present system on the basis of the mass balance is the reaction with NO. Donaruma and Carmody⁵⁶ studied the reaction of nitrosocyclohexane dissolved in cyclohexane with NO at pressures of 1 to 6 atmospheres and 25° to 50°. They observed that the major products were the nitrate, nitrite and nitro compounds of cyclohexane. They also found traces of carbonyl compounds and other nitrated products.

Batt and Gowenlock⁵⁷ studied the isomerization of CH_3NO in the gas phase. They found that NO increased the rate of disappearance of CH_3NO .

In some work more closely related to radiation chemistry Burrell⁵⁸ studied the effect of 6-MEV electrons from a linear accelerator on a solution of nitric oxide in cyclohexane and in the temperature range 25° to 120°C. The first step was formation of a cyclohexyl radical followed by combination with NO, and then further reactions of the nitrosocyclohexane with more NO.

Recently the reactions of NO with methyl radicals produced by photolytic decomposition of organic compounds has been studied.^{2,54}

(55) A. Maschke, B. S. Shapiro, and F. W. Lampe, J. Am. Chem. Soc., **86**, 1929 (1964).

(56) L. G. Donaruma and D. J. Carmody, J. Org. Chem., **22**, 635 (1957).

(57) L. Batt and B. G. Gowenlock, Trans. Faraday Soc., **56**, 682 (1960).

(58) E. J. Burrell, Jr., J. Phys. Chem., **66**, 401 (1962).

The work using nitromethane as a source of methyl radicals was described in the Historical Review Chapter. Nitrosomethane, a product along with formaldehyde, was completely eliminated when a large excess of NO was added. The addition of a small amount of NO, however, led to the formation of more nitrosomethane than when nitromethane was photolyzed alone. This effect caused by a small amount of NO may be responsible for the increase in $G(\text{CH}_3\text{NO})_2$ at 0° and 25° for absorbed doses less than about 1×10^{22} e.v. in the present work. (See Figures 26, 28).

A mechanism has been proposed to account for the products and the observed kinetics of the reaction of aliphatic nitroso compounds with nitric oxide.^{56,58} Here it was found that the reaction was first order with respect to the nitroso compound and second order with respect to nitric oxide. In analogy to the reaction of nitrosobenzene with NO to form benzene diazonium nitrate, an unstable diazonium intermediate had been proposed. The mechanism is given below.

In this sequence of reactions, (39c) is considered to be the rate controlling step. In the present work there is some experimental evidence for the above reactions.

First, there is a dark reaction that produced N_2 , CH_3ONO , and CH_3ONO_2 , presumably by the slow decomposition of $\text{CH}_3(\text{NO})_3$. Second, there is a decrease in the concentration of $(\text{CH}_3\text{NO})_2$ as the other products increase rapidly at larger doses. Third, there is an almost linear increase in the concentration of dimer at 0° where the concentration of NO remains small.

Furthermore, there are some other observations that may be made. $\text{G}(\text{NO})$ can only increase at 25° , if its gross rate of formation is greater than that of nitrosomethane. Conversely the nitrosomethane concentration can only decrease if its rate of decomposition exceeds that of formation. Otherwise, a steady state concentration for both CH_3NO and NO must occur, because the source of both species, CH_3NO_2 , may be assumed to remain constant for such small conversions as were obtained in this study.

Figure 13 shows that the experimental evidence is somewhat

uncertain on this point, although a decrease in concentration of dimer seems to be favored as the dose increases beyond 1×10^{22} e.v. Eventually, however, the nitrosomethane will reach some small steady state concentration as the NO concentration gets even larger.

Looking at this problem of the relationship of $G(\text{CH}_3\text{NO})_2$ to $G(\text{NO})$ from another angle one can see that $G(\text{NO})$ can increase only if CH_3NO disappears by some other means than its reaction with NO, or if $G(\text{NO})$ is greater than $G(\text{CH}_3\text{NO})$.

There is another way in which nitrosomethane may disappear and that is isomerization to formaldoxime. In the gas phase it was found that at room temperature isomerization is less important than dimerization.⁵⁴ However, in solution the reverse situation may be more important as was suggested earlier (p.100).

To study the secondary reactions of nitrosomethane more closely, a simplified version of the reaction of NO with CH_3NO was set up on an analog computer. Also included was the isomerization to formaldoxime. Electronic circuits were set up for the following equations.

The differential equations are:

$$\frac{d[\text{CH}_3\text{NO}]}{dt} = [\text{CH}_3\text{NO}_2]k_A - [\text{CH}_3\text{NO}][\text{NO}]^2k_1 - [\text{CH}_3\text{NO}]k_2$$

$$\frac{d[\text{NO}]}{dt} = [\text{CH}_3\text{NO}_2]k_A - 2[\text{CH}_3\text{NO}][\text{NO}]^2k_1$$

One other simplifying, but easily justifiable, assumption was made, i.e., that the conversion of nitromethane into products was small. In this way the product $[\text{CH}_3\text{NO}_2]k_A$ was made a constant, k' . Thus, it was found that when the rate constant for isomerization k_2 was small compared to k' and k_1 , the concentrations of CH_3NO and NO achieved a stated state. When the constant k_2 was larger than k' and k_1 , the concentration of CH_3NO went through a maximum and the concentration of NO showed a continual increase with time. These results are shown in Figure 29.

Nitrogen is a product of the reaction of NO with CH_3NO as (41) and (42) show. Thus it is a measure of these reactions, provided no other reaction produced N_2 . If this assumption is made, then at the maximum concentration of nitrosomethane dimer, and also assuming that $G(\text{CH}_3\text{NO})_2 = 2G(\text{CH}_3\text{NO})$, we have $G(\text{CH}_3\text{NO}) = G(-\text{CH}_3\text{NO})$.

The maximum value for $G(\text{CH}_3\text{NO})_2$ observed, is 1.3. At $G(\text{CH}_3\text{NO})_2 = 0$, $G(\text{N}_2) = 0.28$. Then

$$2G(\text{CH}_3\text{NO})_2 = G(-\text{CH}_3\text{NO}) \text{ (by reaction with NO)} + G(-\text{CH}_3\text{NO}) \text{ (by isomerization and other means)}$$

$$(2)(1.3) = 0.28 + G(-\text{CH}_3\text{NO})_1$$

$$G(-\text{CH}_3\text{NO})_1 \approx 2.3$$

This indicates again that the rate of isomerization or other means of decomposition is much greater than the reaction with NO . This is consistent with the results of the analog computer.

A — $k_2 < k_1$ and k' , B — $k_2 > k_1$ and k'

Figure 29.—Analog computer curves for CH_3NO and NO formation.

$G(\text{NO})$ can also be estimated in this way, since $G(\text{NO}) = 2G(\text{N}_2) + G(\text{NO})_{\text{observed}}$. Hence

$$G(\text{NO}) \approx 0.56 + 0.30 \approx 0.86 \text{ at } G(\text{CH}_3\text{NO})_2 = 0$$

Finally the effect of added NO_2 may be considered. Here it was found that the amount of nitroso dimer formed was much reduced. This is not surprising in view of the large amount of NO formed during the radiolysis of the solution, which would destroy the nitrosomethane.

Methyl nitrite and methyl nitrate

Methyl nitrite was the third major initial product at 25° . $G(\text{CH}_3\text{ONO})$ at small doses is a constant, 1.1, but at doses greater than 1×10^{22} e.v. it increases, becoming 7.4 at 1.8×10^{22} e.v. The same situation applies at 0° except that $G(\text{CH}_3\text{ONO})$ is 0.60 initially and at 1.8×10^{22} e.v., it is 2.9. These data are shown in Figures 26 and 28.

The formation of methyl nitrite has been attributed to several reactions. In the photolysis of liquid nitromethane where it was almost the only product observed, its formation was attributed to (31).¹⁸

To explain the absence of other products, especially NO which was an important product in the gas phase photolysis, it was suggested that the methyl nitrite formed in the gas phase was excited and dissociated according to (47).

Figure 30.--The influence of dissolved water on Methyl nitrite G-values at 25°C.

In the liquid the CH_3ONO could be stabilized by collisional deactivation. Another possibility is that even if (47) does occur, cage effects could lead to recombination before the radicals were able to diffuse away.

Methyl nitrite may also be made by the action of nitrous acid or N_2O_4 on methanol.³⁰

Equation (49a) represents the standard method of preparation in which the nitrous acid is produced by the action of sulfuric acid on a sodium nitrite solution also containing methanol. At room temperature the methyl nitrite is gaseous and escapes, driving the reaction toward the right. In nitromethane very small concentrations are involved and the methyl nitrite is soluble enough to be determined chromatographically. Nitrite esters are easily hydrolyzed in water. Without more information as to how readily methyl nitrite decomposes to the alcohol in nitromethane not much can be said about (49b). It would seem, though, that if (49b) did occur, appreciable amounts of methanol would have been detected, rather than the mere trace amounts that were found. This probably applies to (24) also. Thus, it seems likely that (31) is the source of methyl nitrite.

In common with several other products $G(\text{CH}_3\text{ONO})$ increases with dosage as mentioned above. Should $G(\text{CH}_3\text{ONO})$ increase further or even remain at 7.4 as the dose increases it would be possible to consider the methyl nitrite the sole major product at high dosages in agreement with the findings of Rebbert and Slagg for the photolysis of liquid nitromethane. Therefore, it is interesting to compare the per cent conversion of nitromethane into products in the two studies. Rebbert and Slagg do not give a value for the per cent conversion of the liquid. In their work with gaseous nitromethane they obtained a minimum conversion of 0.01%. In the present work based on the observed products containing carbon, the minimum mole fraction of carbon observed was 2.1×10^{-5} at 0° and 4.0×10^{-4} at 25° . (See Table 8). Hence, the minimum observed conversion was about 0.02% at 25° and 0.1% at 0° . Thus, the two studies are roughly comparable with respect to conversion, assuming that the minimum decomposition was the same in the liquid as the gas in Rebbert and Slagg's work.¹⁸

The next problem is to account for the increase in $G(\text{CH}_3\text{ONO})$. Reaction (45), resulting from the decomposition of the complex, $\text{CH}_3\text{-N=N-ONO}_2$, is one source, but here again the amount of nitrogen produced precludes this as being a major source of CH_3ONO . In other words just as the disappearance of $(\text{CH}_3\text{NO})_2$ cannot be mainly due to reactions (39), (41), (42), so the appearance of methyl nitrite cannot be attributed mainly to this source.

What is needed, then, is not only decomposition of $\text{CH}_3\text{N}_2\text{ONO}_2$ to give CH_3 radicals and NO_2 as a source of methyl nitrite, but some sort of subsequent decomposition of CH_3NO_2 to give CH_3ONO . This

would account for the formation of CH_3ONO in the dark reaction. In other words, intermediates from the decomposition of CH_3NO may initiate a short chain decomposition of nitromethane leading to the formation of methyl nitrite.

An alternate approach to this problem is to assume that the formation of CH_3NO interferes in some way with the formation of CH_3ONO . Then, when nitrosomethane is removed by isomerization or some other means, the rate of formation of methyl nitrite can increase.

In a qualitative experiment a solution of NO and a trace of cis nitrosomethane dimer in nitromethane was prepared. NO_2 was also present as an impurity. The solution was allowed to stand for a week at 25° . When the vessel was opened methyl nitrite was found to be present. Other solutions in which nitrosomethane or NO (plus NO_2) were dissolved alone in nitromethane showed no formation of methyl nitrite. This suggests that the nitrosomethane monomer is a precursor of at least a portion of methyl nitrite.

Methyl nitrate is also produced by the reaction of NO with CH_3NO according to equations (43a), (43b), and (47). And like CH_3ONO , $G(\text{CH}_3\text{ONO}_2)$ shows an increase after $G(\text{CH}_3\text{NO})_2$ becomes zero.

However, methyl nitrate formation differs in several respects from that of methyl nitrite. First, $G(\text{CH}_3\text{ONO}_2)$ remains much smaller than $G(\text{CH}_3\text{ONO})$ at all doses. Second, $G(\text{CH}_3\text{ONO}_2)$ is independent of temperature. Third, whereas the formation of methyl nitrite seems to be almost eliminated by the addition of NO_2 , CH_3ONO_2 is unaffected, at least at doses less than 1×10^{22} e.v.

Since methyl nitrite appears to be formed by a free radical

mechanism, this suggests that the ionic reaction, (43b), is mainly responsible for the formation of methyl nitrate.

Minor products, CO₂

The minor products that have not yet been discussed are CO₂, N₂O, C₂H₆, and CH₄.

Carbon dioxide is interesting because it behaves in miniature like methyl nitrite. In other words G(CO₂) is much smaller than G(CH₃ONO) at all doses at the same temperature, but in other respects their behavior is similar. G(CO₂) remains small and constant at 0°C. G(CH₃ONO) only increases near the highest doses used. At 25°C G(CO₂) remains constant until after G(CH₃NO)₂ becomes zero, when it rapidly increases. (See Figure 27). This is also true of CH₃ONO. Similarly, based on initial G-values of 0.07 and 0.16 at 0° and 25° respectively, the activation energy for CO₂ formation is about the same as for methyl nitrite, approximately 5 kcal/mole. Also like methyl nitrite CO₂ is produced in the dark reaction.

In previous work CO₂ has often been observed. Its formation has been attributed to the oxidation of nitromethane,⁴ a reaction between CO and NO₂,¹ and the oxidation of methyl radicals.¹⁷

The first of these suggestions is too general to be of much help. The second,

is not likely in the radiolytic system, because G(CO) remains constant with dose and temperature variation, whereas G(CO₂) changes.

The third may be of some importance, but before discussing it,

the source of CO_2 from other radiolysis studies should be considered. In radiation chemistry CO_2 most often results from the decomposition of compounds containing the $\text{-C} \begin{smallmatrix} \nearrow \text{O-} \end{smallmatrix} = \text{O}$ group, that is, acids and esters. For instance in the gamma radiolysis of acetic acid Johnsen⁵⁹ found $\text{G}(\text{CO}_2)$ was almost twice that of any other product.

There are some indications in the present work that compounds containing at least the C=O group, other than CH_2O are present. This is based on the infrared analysis of the residue. (See Figure 9 and the discussion of the qualitative analysis for cis nitrosomethane dimer.) Thus, the radiation decomposition of a carbonyl compound, perhaps an acid, may in part be responsible for the formation of CO_2 . This cannot be the only means of forming CO_2 , because it is also produced in the dark reaction where there is no radiation.

What is needed, then, is a slow reaction--the reaction of NO with CH_3NO . Methyl nitrite is a product of this reaction and CO_2 behaves like methyl nitrite. Therefore, it seems likely that CO_2 is produced in some manner by this reaction. In this connection it is interesting to note that Donaruma and Carmody observed traces of carbonyl compounds when NO reacted with cyclohexane in the presence of a catalyst.

This leads us back to the oxidation of methyl radicals suggested by Nicholson. Since methyl radicals are produced in (41), oxidation may indeed be the way in which CO_2 is formed, with NO_2 or NO_3 the oxidizing species.

(59) R. H. Johnsen, *ibid.*, 63, 2041 (1959).

Nitrous oxide

Nitrous oxide is a very minor product which probably arises from the decomposition of the other oxides of nitrogen. For instance nitric oxide gas under pressure reacts to form N_2O .⁶⁰

Thus the increase in $G(NO)$ at 25° could lead to an increase in $G(N_2O)$. Nitrous oxide may also arise from the reaction of nitrous acid with hydroxylamine, the hydroxylamine coming in turn from the hydrolysis of formaldoxime.⁶⁰

There is also the possibility that nitrous oxide results from (23), the decomposition of the HNO radical.

Ethane

$G(C_2H_6)$ remains constant with dose throughout the whole dose range observed. There is a temperature effect, $G(C_2H_6) = 0.03$ at 0° , 0.06 at 25° , but with such small G -values, it is difficult to tell how much of this is real and how much experimental error.

Ethane has been mentioned as a product in most studies of nitromethane decomposition. Its formation is attributed to radical combination.

The very small G -values for C_2H_6 compared to CH_3ONO suggest

(60) E. Barnett and C. L. Wilson, "Inorganic Chemistry, A Text-book for Advanced Students," Longmans Green and Co., London, England 1953, pp. 338, 342, 351.

cage effects must be important in nitromethane or else the reaction,

must occur much more readily in competition with (53). Strong cage effects would mean that CH_3 radicals would collide with NO_2 formed in the same cage much more frequently than they would diffuse away to collide with another CH_3 radical from a different cage. This could rationalize the higher $G(\text{C}_2\text{H}_6)$ at 25° , because cage effects become weaker at higher temperatures as the kinetic energy of the molecules increases and the radical more readily diffuses.

Methane

$G(\text{CH}_4)$ follows the same course at 0° and 25° although there is some experimental uncertainty about this as Figure 23 shows. Like many of the other products it remains constant at 25° until after $G(\text{CH}_3\text{NO})_2$ becomes zero.

Methane is probably produced by an abstraction reaction.

It is a product, albeit a minor one, of the dark reaction. This also supports an abstraction reaction because methyl radicals are produced by (41).

Abstraction reactions in which methyl is the abstracting group generally have an activation energy of 5 to 10 kcal/mole.⁶¹ The

(61) S. N. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pp. 296-8.

absence of an observed temperature effect may be due to experimental errors or it may simply be due to the lack of knowledge concerning the activation energy for the overall reaction, that is, reactions (39), etc.

Future work

By now it should be apparent, although it is hoped not too painfully so, that much work remains to be done. The present study has been mainly concerned with exploratory work on the nitromethane system; that is, it has been mainly concerned with finding suitable experimental techniques for discovering and analyzing the products. Only secondarily have mechanisms of product formation been considered.

Future work on the liquid should include more studies at doses extended beyond 2×10^{22} electron volts, temperatures other than 0° and 25° , and dose rates differing from the present study. The addition of scavengers should also be tried. The gas should also be irradiated to obtain a better comparison with the mass spectrometer.

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