Thermolysis of Nitromethane in Pressurized Supercritical Media

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The decomposition of supercritical nitromethane at liquid-like densities gives HCN and CO_2 as the principal carbon-containing products whereas at low pressure CH_4 and CO predominate. The decomposition is powerfully accelerated by increased density, and a contact ion-pair transition state is inferred. The activation volume is −85 mL/mol. A new method of measurement is described. Various lines of evidence indicate a shift from homolysis at low pressure to rearrangement in dielectric media.

Introduction

The chemistry of nitromethane is interesting not only because of its myriad uses in organic synthesis as a solvent and as a reagent for condensations and Michael additions but also because it is the archetype of an important class of high explosives. Its technical applications as an explosive are somewhat specialized because it is a liquid, but its high power and low sensitivity are frequently advantageous. It is well suited to our purpose of studying the fundamental processes involved in explosive decomposition because of its structural simplicity. The chemical, physical, and thermodynamic properties which are relevant to its use as an energetic material are described in a review.[1]

The pyrolysis of nitromethane at pressures up to 0.2 atm and temperatures from 305 to 440 °C has been painstakingly investigated by Crawforth and Waddington.[2] The reaction rate is pressure-dependent up to 0.2 atm where it becomes first order with reaction rate constant equal to $10^{14.1}\exp(-232\ \mathrm{kJ}/RT)\ \mathrm{s}^{-1}$. By studying the reverse reaction O'Neal and Benson[3] found $10^{15.6}\exp(-247\ \mathrm{kJ}/RT)$ which agrees reasonably well. The products in order of abundance are carbon monoxide, methane, water, nitrogen, and carbon dioxide together with small amounts of hydrogen cyanide and oxides of nitrogen. It seems highly probable that methane is formed from methyl radicals by hydrogen abstraction and that the methyl radicals are generated by homolysis of the carbon–nitrogen bond:

$$CH_3NO_2 \rightarrow CH_3^{\bullet} + NO_2 \quad (1)$$

$$CH_3^{\bullet} + CH_3NO_2 \rightarrow CH_4 + {}^{\bullet}CH_2NO_2 \quad (2)$$

The observed yield of methane was 60–70% of the maximum allowed by eq 1 and 2. If the rate-limiting step is (1), the activation energy should be equal to the bond dissociation energy for which values of 248 and 251 kJ have been cited.[4,5] The experimental value of 232 kJ agrees satisfactorily.

The potential energy surface for rearrangements of nitromethane has been calculated by McKee[6] and Dewar,[5] but their results strongly disagree. Dewar finds that the preferred pathway for decomposition of nitromethane involves rearrangement to methyl nitrite followed by elimination of nitroxyl (3).

$$CH_3NO_2 \rightarrow CH_3ONO \rightarrow CH_2O + HNO \quad (3)$$

The activation energy for rearrangement is 54 kJ lower than that for homolysis. By this scheme it is difficult to account for the high abundance of methane among the products as noted above. McKee, on the other hand, finds that concerted rearrangment to methyl nitrite would have a barrier which is 130 kJ higher than the dissociation energy of the carbon–nitrogen bond (1). His potential energy surface has a ridge which separates the concerted path from that of radical dissociation and recombination. If he were correct, one would not expect to find reaction intermediates derived from methyl nitrite.

In a recent study of dissociation of nitromethane in a molecular beam by multiple absorption of IR photons (1078 cm^{-1}), Wodtke, Hintsa, and Lee[7] found CH_3O among the products which they ascribed to the reaction

$$CH_3NO_2 \rightarrow CH_3ONO \rightarrow CH_3O^{\bullet} + NO \quad (4)$$

They estimated that this reaction runs parallel to direct homolysis (1) with a branching ratio (homolysis/rearrangement) of 0.6 ± 0.2. It therefore appears that the difference in barrier height is very small under the conditions of the molecular beam experiment.

The preponderance of evidence[2,7,9] suggests that homolysis is the chief mode of decomposition of nitromethane in the vapor phase at low pressure. Mechanisms having nonpolar transition states are favored under these conditions, although some vapor-phase reactions of polar character have been reported. An example is the elimination of HCl from alkyl chlorides[8] which is thought to have a tight-ion-pair or semi-ion-pair transition state. One of the many pieces of evidence is the occurrence of Wagner–Meerwein rearrangements. With the thought that pyrolysis of nitromethane might shift from a free-radical path to a polar mechanism in a medium having a significant dielectric constant, we undertook a study in which the neat supercritical vapor and mixtures with other supercritical vapors are compressed to densities approaching 1 g/cm^3. Aside from its intrinsic interest, the decomposition in a dense medium bears a closer relation to the phenomena which occur during the initiation of detonation. One possible ancillary benefit of such a study might be a better understanding of the action of sensitizers. The literature contains one suggestion of a shift in the contributions of competing reaction paths as pressure is increased. Mueller[9] has found that even moderate pressures near 17 atm cause a significant increase in the ratio of hydrogen cyanide to methane. The increased yield of hydrogen cyanide was attributed to the ascendancy of reaction (5) over (1), but no explanation was offered for the effect of pressure on the ratio of reaction rates. The

$$CH_3NO_2 \rightarrow CH_3NO + O \rightarrow HCN + H_2O + O \quad (5)$$

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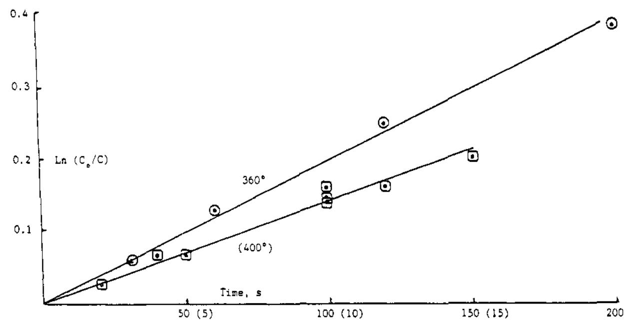

Figure 1. First-order rate plots for neat nitromethane at 360 and 400 °C.

Table I. Effect of Density on Rate of Decomposition of Nitromethane

T = 400 °C		T = 360 °C	
d, g/cm^3	k, s^{-1}	d, g/cm^3	k, s^{-1}
0.05	0.0020	0.45	0.00093
0.12	0.0021	0.65	0.0022
0.30	0.0027		
0.34	0.0055		
0.43	0.0070		
0.56	0.141		

reported total rate was ten times greater than the rate we calculate from Crawforth and Waddington's activation parameters for the same temperature. This suggests that the alteration in rate ratio is due more to acceleration of a competing reaction than suppression of (1).

Results and Discussion

Samples of nitromethane in the milligram range were sealed in glass capillary tubes and reacted at temperatures up to 400 °C and times down to 1 s. Pressures occasionally rose to hundreds of bars, and some of the tubes burst, but the small scale reduces the hazard. In all cases the vapor was supercritical (T_c = 315 °C). At densities above 0.10 g/cm^3 the products consisted mainly of hydrogen cyanide, carbon dioxide, water, and nitrogen in roughly stoichiometric proportions together with small amounts of carbon monoxide and nitrous oxide and traces of cyanogen and methane. At lower densities methane was formed in significant amounts as noted by earlier workers.[2,9] At a density of 0.05 g/cm^3 the carbon-containing product proportions were (mole percent) HCN 49, CO_2 38, CH_4 13. We concur with Mueller in ascribing the change in product composition to an effect of density on the relative rates of competing reactions.

The effect of density on the reaction rate is shown in Table I. A first-order rate law is assumed, and the rate constant is based on the rate of appearance of the two principal carbon-containing products, HCN and CO_2. It is assumed that the number of moles of CH_3NO_2 consumed is equal to the sum of the number of moles of HCN and CO_2 found in the partially reacted samples. A good fit to a first-order rate law was found as shown in Figure 1, but since the reaction was followed only up to 20–30% completion in order to prevent excessive pressure development, one must admit the possibility that the true order could be higher. The pyrolysis of nitromethane in benzene or acetonitrile, however, obeys a first-order rate law up to 50% reaction and therefore we believe that the phenomenal increase in reaction rate with density is a medium effect and not the result of bimolecular processes. This conclusion is reinforced by the absence of a primary H/D kinetic isotope effect which will be discussed later. At the lowest density used (0.05 g/cm^3, P = 50 atm) the rate is 10 times higher than that calculated from the data of ref 2, and the ratio of HCN to CH_4 shows a comparable increase. We conclude that homolysis, (1), which produces CH_4 is overtaken by another reaction which produces HCN. The most plausible explanation is that the dominant reaction at high density is rearrangement to methyl nitrite, (3), as suggested by Dewar.[5] The decomposition of methyl nitrite would produce reducing agents such as formaldehyde shown in (3). The formation of hydrogen cyanide can be explained by reduction of nitromethane to nitrosomethane by formaldehyde or any of the reactive intermediates between formaldehyde and carbon monoxide or dioxide. Formaldehyde is not found among the products, and we presume it is reduced to a very low level through oxidation by nitromethane and nitrous acid and their degradation products. The proposed sequence of steps is shown in Scheme I.

Scheme I. Pyrolysis of Nitromethane in Dielectric Media

$$CH_3NO_2 \rightleftharpoons \underset{\text{contact ion pair}}{CH_3{}^{+}NO_2{}^{-}} \longrightarrow CH_3ONO \longrightarrow CH_2O + HNO_2$$

$$CH_3NO_2 \xrightarrow{[H]} CH_3NO \longrightarrow CH_2{=}NOH \longrightarrow HCN + HOH$$

$$CH_2O \xrightarrow{[O]} CO + CO_2$$

$$HNO_2 \xrightarrow{[H]} N_2O + N_2$$

The increase of rate with density can be linked to the increase in dielectric constant. The change in free energy of activation for a reaction generating a dipole moment, μ, in a cavity of radius r in a medium of dielectric constant ϵ relative to reaction in a vacuum is given by the following equation due to Kirkwood:[10]

$$\Delta\Delta G^{\pm} = N_0\mu^3 (\epsilon - 1)/r^3(2\epsilon + 1) \qquad (6)$$

If we estimate that μ = 5 D, $r = 2.5 \times 10^{-8}$ cm, and ϵ = 3, the rate factor, exp $(\Delta\Delta G^{\pm}/RT)$, at 673 K would be approximately 10^2.

The activation energy for pyrolysis of nitromethane at a density of 0.60 g/cm^3 in the temperature interval from 360 to 400 °C is 170 kJ, and the activation entropy is $-5.5R$. Both the low activation energy and negative activation entropy are appropriate to a transition state conceived as a solvated ion pair. A homolytic transition state, on the other hand, demands an activation energy nearly equal to the bond dissociation energy (250 kJ) and a positive entropy change. Additional evidence for a polar transition state is presented in the following section.

By measuring the effect of pressure on reaction rate constants it is possible to evaluate the difference in molar volume between transition states and reactants. The relation between activation volume, $\Delta V^{\pm}$, and the pressure effect is given by eq 7. It is surprising in view of its simplicity and fundamental nature that the utility of eq 7 is not widely known. In recent years it has been helpful in characterizing transition states and clarifying reaction mechanisms. Hundreds of cases are discussed in a current book by Isaacs.[11]

$$\Delta V^{\pm} = -RT(\delta \ln k/\delta P)_T \qquad (7)$$

The volume of the dipolar transition state shown in Scheme I would be affected to a small degree by elongation of the carbon–nitrogen bond, but the dominant feature is electrostriction of the surrounding molecules which results

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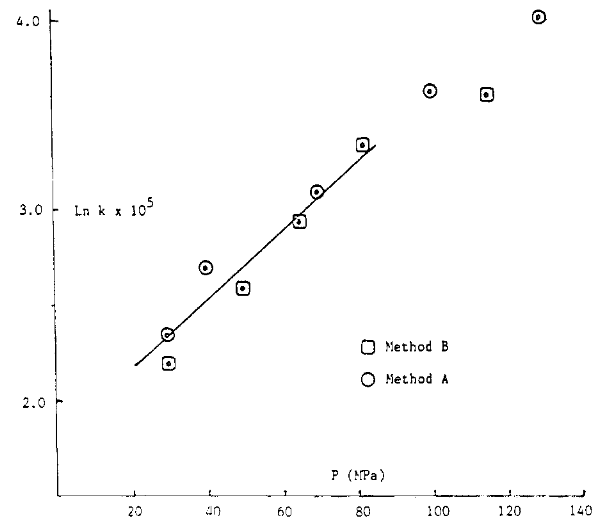

Figure 2. Ln of first-order rate constant (s^{-1}) vs pressure for 20% (vol) nitromethane in acetonitrile at 315 °C.

in a large negative volume change. The importance of the electrostriction effect is seen in S_N1 reactions of neutral substrates which have activation volumes ranging from −15 to −25 mL/mol at ordinary temperature. A very close analogy to the rate-determining part of Scheme I is the rearrangement of benzhydryl thiocyanate to the isocyanate[12] which has an activation volume of −12 mL in a mixed aqueous medium. At higher temperatures and in nonaqueous solvents the electrostriction becomes much more pronounced. The displacement reaction of 2-bromonaphthalene with piperidine at 189 °C, for example, has a zwitterionic transition state and an activation volume of −68 mL.[13]

An electrostatic model for volume of electrostriction by dipoles has been proposed by Heydtmann.[14] By application of the relation $(\delta G/\delta P)_T = V$ to eq 6, one obtains

$$\Delta V^{\pm} = \frac{3N_0\mu^2(\delta\epsilon/\delta P)_T}{r^3(2\epsilon + 1)^2} \qquad (8)$$

Since the values of the parameters are very uncertain, the equation is not quantitatively useful, but qualitative conclusions can be drawn. The supercritical vapor media used in this study have low dielectric constants compared to ordinary solvents (especially aqueous mixtures) at ordinary temperature, and the pressure coefficients of their dielectric contents are larger owing to the greater compressibility of these fluids. The combined effect of the two factors will give the activation volume a large negative value, and we should perhaps anticipate a greater magnitude than any previously observed.

Figure 2 is a plot based on eq 7 for pyrolysis of nitromethane in acetonitrile. The activation volume calculated from its slope near the origin is −85 ± 5 mL/mol. Obviously a contraction of this magnitude can only result from compression of a number of surrounding molecules by an intense electric field. It is more than twice as large as the volume change on dissolving an electrolyte in a nonaqueous solvent under ordinary conditions, but supercritical acetonitrile is more compressible even at pressures up to a kilobar than ordinary liquids. It should be emphasized that the data Figure 2 begin at pressures which give liquid-like densities. At lower pressures the slope would undoubtedly be much greater, but comparison to ordinary liquid-phase reactions would no longer be appropriate. The use of benzene as a solvent gave results similar to those of acetonitrile, but relatively few points were measured.

It should not be supposed that the large negative activation volume associated with the decomposition of nitromethane will be typical of all explosive compounds or even all compounds containing the nitro group. Work in progress shows that the decomposition of nitrate esters is retarded by pressure as expected for a homolytic process.

Nitromethane and nitromethane-d_3 were dissolved in four parts by volume of acetonitrile and reacted at a temperature of 315 °C under a pressure of 170 atm. The rate constants were $k_H = 5.5 \times 10^{-5}\ s^{-1}$, $k_D = 4.7 \times 10^{-5}\ s^{-1}$ and the isotope effect is 1.2. Clearly there is no primary effect, and the value is probably consistent with the α secondary effect expected for the contact ion pair shown in Scheme I. A larger value would be expected at room temperature, but for 315 °C it seems reasonable. The possibility of a bimolecular process involving hydride transfer can probably be dismissed.

An equimolar mixture of nitromethane-d_3 and benzene was decomposed at a low density, 0.08 g/cm^3, and a high temperature, 390 °C, in order to promote homolytic decomposition. Based on unreacted benzene, we found the following percentages of products: $PhCD_3$, 0.3; PhOH(D), 1.5; PhCN, 0.2; $PhNO_2$, 1.8. They give evidence for the intermediacy of $CD_3^{\bullet}$ and NO_2 as shown in eq 1, together with small amounts of $NC^{\bullet}$ and perhaps $HO^{\bullet}$. Cyanogen was mentioned earlier as a minor product. When the experiment was repeated using a density of 0.50 the radical-derived products were not found owing to the acceleration of the polar mechanism.

Experimental Section

Capillaries for Neat Nitromethane. Pyrex tubing was drawn into capillaries having approximately 0.4 mm outside diameter and 0.25 mm inside diameter. A 50-mm length was sealed at one end and placed upside down in a tube which was then evacuated. A small quantity of nitromethane was allowed to enter through a valve, and air was admitted from above which caused the capillary to fill completely. The capillary was removed and warmed to evaporate as much nitromethane as desired. The mass of nitromethane was determined by weighing the capillary empty and loaded. The average sample size was 1 mg. The open end of the capillary was sealed by drawing it off in a flame. The density of the vapor to be generated in the capillary was calculated by multiplying the room-temperature density of nitromethane by the ratio of the filled length to the total length of the capillary. The density could be predetermined to ±0.02 g/cm^3 by control of the evaporation step.

Heating Bath for Neat Nitromethane. A cylindrical well measuring 1 cm by 8 cm was drilled in an aluminum block and filled with lead. The block was fitted with a steady heater, a control heater, a thermostatic controller, and a platinum resistance thermometer. Temperature measurement and control was within 1°. The capillary tubes containing nitromethane were completely immersed in the molten lead at various temperatures up to 400 °C for times ranging down to 1 s. The operation was conducted behind a safety shield in a fume hood because up to 20% of the tubes would burst under the most severe conditions of temperature and reaction time. The thermal equilibration time (10 τ) can be estimated from the thermal diffusivity (D) and the thickness of the glass (x) by taking the relaxation time (τ) from the relation

$$x^2 = 2D\tau \qquad (9)$$

We conclude that thermal equilibrium would be attainded in less than 0.1 s and that quenching would also be very fast.

Analysis of Partially Decomposed Nitromethane by FTIR. Capillaries which had been heated were placed in a side arm of a specially designed evacuable IR gas cell. A sealed plunger was

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used to break the capillary and discharge its contents into the evacuated cell. The spectrum was scanned at 2 cm^{-1} resolution, and absorbances were recorded at the following frequencies (cm^{-1}): 3016 (CH_4), 2360 (CO_2), 2214 (N_2O), 2173, 2169 (CO), 713 (HCN). Peaks due to unreacted nitromethane were not recorded. Calibration plots obtained by spectral analysis of known amounts of each gas were used for quantitation. At densities above 0.10 g/cm^3 the only significant carbon-containing products were CO_2 and HCN. For the purpose of calculating rate constants, it was assumed that the sum of the number of moles of CO_2 and HCN is equal to the number of moles of CH_3NO_2 consumed.

Semiquantitative Analysis by GC/MS. Partially reacted sample tubes were broken on the inside of a closely fitting external tube which was closed at one end and fitted with a hypodermic needle at the other. The gases passed directly into the inlet port of the GC/MS instrument. In addition to unreacted nitromethane and the products identified by FTIR we found H_2O, N_2, and a trace of $(CN)_2$. No products boiling higher than nitromethane were found.

Measurement of Reaction Rates in Solution at a Known Pressure. Method A. Benzene and acetonitrile were chosen as solvents because they are stable under the reaction conditions and show no evidence of reaction with nitromethane or its degradation products except under low-density homolytic conditions as noted above. Another criterion which becomes crucial in connection with method B is that accurate PVT data for benzene[15] and acetonitrile[16] have been reported. The solutions contained 20% by volume of nitromethane. Approximately 30 μL of solution was placed in a 2-mm melting point capillary which had a flared opening. A 3-mm length of PTFE "spaghetti" was pressed into the mouth, and a tapered glass fiber was inserted in the central hole of the "spaghetti" to expand it snugly against the glass wall of the capillary. This formed a piston to transmit pressure from an external fluid (heptane) to the reaction mixture. The pressure vessel was a 15-cm length of $^1/_4$ in. stainless steel pressure tubing of 2.5 mm i.d. which had a standard high-pressure coned fitting at one end and a miniature conical plug seated by a 10–32 screw at the other end. The glass capillary containing the sample was placed in the pressure vessel which was then closed and pressurized by a hand operated pump. The heater was an aluminum block equipped for controlled heating to 400 °C as previously described. It could be moved vertically on a rail in order to lower it onto the pressure vessel which entered a close-fitting blind hole in the heating block. Thermal equilibration was attained in about 1 min, and reaction times were usually longer than 20 min. At the end of the reaction period the heater was withdrawn upward and the heater was rapidly quenched. Pressure was maintained while the reactor was cooled to −70 °C in order to minimize problems due to the dissolved gases which would frequently expel the piston after removal of the glass capillary. The reaction mixture was analyzed by capillary GC using a flame ionization detector. The solvent was used as an internal standard for determining the fraction of unreacted nitromethane. An acceptably small quantity of heptane pressurizing fluid was usually also present.

Method B. Since the conditions are severe even for PTFE and since leakage during the reaction was not completely suppressed and since dissolved gases created problems in handling, we explored the possibility of using sealed glass containers. Knowledge of the density makes it possible to determine the pressure from PVT data which are available for several suitable solvents. By themselves the capillaries will not withstand the highest pressures needed (130 MPa), but external pressurization enables them to do so. Sealed melting point capillaries rarely implode under an excess external pressure of 100 MPa. With the data of ref 16 we determined the pressures of acetonitrile solutions of nitromethane from the measured ullages at room conditions and compared reaction rates with those obtained from the moving piston device at the same pressures. This empirical validation was considered necessary because otherwise we would be forced to rely on the accuracy of the PVT data and would face uncertainties arising from the effect of the solute on the PVT relations as well as corrections for thermal expansion and mechanical deformation of the capillary. Figure 2 presents results obtained by method A and method B on a single graph and gives us confidence that the pressures derived from PVT data are reliable.

Experimental Errors. The digital display for the platinum resistance thermometer was checked by an absolute measurement of resistance by use of the freezing point of lead. Temperatures appear to be reliable to 1°. The activation energy, 170 kJ, for neat nitromethane at $d = 0.60$ is uncertain by about 8 kJ on the basis of temperature measurement and another 8 kJ on the basis of reproducibility of rates. The reproducibility of analyses by capillary GC is within 3% and by FTIR within 5%. The error in rate could possibly amount to 10%. Inspection of Figures 1 and 2 is probably the best basis for judging the reliability of the measurements. In determining activation volumes, it is fortunate that no error results from a constant multiplicative error in rates such as might be caused by an error in temperature or calibration of the FTIR and GC analyses. We would not be greatly surprised if a redetermination of activation volume in an independent laboratory were to give a value as high as −70 mL or as low as −100 mL. No change in interpretation would be required.

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Registry No. CH_3NO_2, 75-52-5; D_2, 7782-39-0.

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Reactions of Weak Carbon Acids under Phase Transfer Catalysis Conditions: Oxidations and Hydrogen–Deuterium Exchange

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The hydrogen–deuterium exchange of very weak carbon acids (p$K_a \leq 38$) under extractive phase transfer catalysis (PTC) conditions is reported. Benzylic hydrogens, hydrogens of several heterocyclic systems [benzo[*b*]furan (**8**), benzo[*b*]thiophene (**9**), thiophene (**10**)], and aromatic hydrogens in di- and trihalobenzene derivatives could easily be exchanged. The reaction was performed in the presence of $(Bu)_4N^+HSO_4^-$ as the PTC catalyst and $NaOD/D_2O$, 60% w/w, as base and the deuterium source. A quantitative autoxidation reaction was performed on benzylic carbons in the presence of air. Of special significance is the nature of the PTC catalyst. The importance of the catalyst counteranion is emphasized.

Phase-transfer catalysis (PTC) has proved itself as a method of choice in a very wide scope of chemical reactions in various areas.[1] Of special significance is the hydroxide ion transfer process, which permits the application of

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