Thermal decomposition of arylnitramines

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The thermal decomposition of various substituted *N*-methyl-*N*-nitroanilines dissolved in indifferent solvents and piperidine has been investigated. Activation volumes and product analyses support evidence that the rate-determining step is the reversible homolysis of the nitramine bond. The activation volumes range from +18 to +36 ml mol^{-1}. A non-linear Hammett relationship is attributed to an increase in secondary caged reactions, namely rearrangement and oxidation. Arylnitramines with electron-donating substituents yield greater amounts of the thermal rearrangement products than those with electron-deactivating groups at ambient pressures. Decomposition of arylnitramines with electron-donating substituents under high pressures (*ca.* 1.2 GPa) favours caged reactions over separative diffusion.

Introduction

Many studies have been reported on the acid-catalysed rearrangement of arylnitramines (Fischer–Hepp) while little effort has been made to investigate their thermal rearrangement. The acid-catalysed rearrangement is to this day not well understood and has been the subject of much controversy. In order to understand better the chemistry of arylnitramines, the simpler non-catalysed rearrangement reaction by thermal decomposition has been investigated.

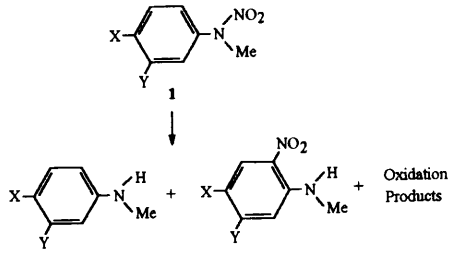
The rearrangement of the simplest arylnitramine, *N*-nitroaniline, by thermal means was first reported by Bamberger and Landersteiner.[1] Its thermal decomposition gives principally *o*-nitroaniline with some *p*-nitroaniline, nitrosobenzene, carbon dioxide and nitrous fumes. No mechanism was given. In another study, Barnes and Hickinbotham found that *N*-methyl-*N*,*p*-dinitroaniline, neat or in dichloroethane, thermally rearranges to give *N*-methyl-2,4-dinitroaniline in high yield; however, rearrangement is effectively quenched by the addition of dialkylphenols to the reaction medium, affording mostly *N*-methyl-*p*-nitroaniline.[2] These reactions were interpreted by them on the basis of homolysis of the nitramine bond, which was later supported by a large positive activation volume of the decomposition of the same compound dissolved in a mixture of toluene and piperidine.[3] Comparable to the above reactions, Banthorpe and Thomas found that *N*-methyl-*N*-nitro-1-naphthylamine rearranges to the 2- and 4-nitro isomers when thermolysed in various solvents at 100 °C or when exposed to UV radiation at 20 °C.[4] In addition to the product analysis, the rate of reaction was qualitatively found to increase with increasing polarity of solvent media. Partly from these solvent effects and the lack of evidence for intermediate radicals, the authors inferred that the nitramine bond undergoes heterolysis to the nitrite ion and methylnaphthylamino cation as the first decomposition step.

In general, the proposed mechanisms of thermal rearrangement were based to a large extent on the thermolysis products. In this study, substituent and pressure effects on the rates of decomposition and yields of rearrangement products of various arylnitramines are reported. At ambient pressure, arylnitramines in solution decompose to their respective parent arylmethylamines, rearrangement and oxidation products.

Results and discussion

Hammett relationship

The Arrhenius parameters of the decomposition of six arylnitramines dissolved in benzene and piperidine (1% by volume) were measured. The additive piperidine acts to scavenge nitrogen oxides and trace acids to preclude the acid-catalysed rearrangement reaction. Table 1 gives the calculated first-order rate constants for each arylnitramine along with their respective substituent constants, σ. These data indicate a sudden sign reversal of the reaction constant, ρ, at *ca.* $\sigma = 0$. For substituents *p*-MeO, *p*-Me and H, ρ° and ρ^{+} were calculated as -4.7 and -1.7, respectively; for substituents H, *p*-Br and *p*-NO_2, ρ° was calculated as $+1.4$. Note that better data correlation is obtained when using σ^{+} values over those of σ° for *p*-OMe, *p*-Me and H substituents. In order to obtain a successful Hammett relation of a series of reactants, the activation entropy should remain fairly constant or vary linearly with activation enthalpy.[5] Compound **1e** (*m*-NO_2) does not have activation entropy and enthalpy values that fit within the range established by the remaining reactants (see Table 2) and was neglected from the calculation of the reaction constant with positive slope. Because of scatter and the few number of substituents studied, these calculated reaction constants must be taken as approximations. The Hammett relationship for these reactions is useful for demonstrating the existence of a



1a X = OMe Y = H
1b X = Me Y = H
1c X = H Y = H
1d X = Br Y = H
1e X = H Y = NO_2
1f X = NO_2 Y = H

Table 1 Substituent and rate constants for various substituted *N*-methyl-*N*-nitroanilines. Rates are calculated for 100 °C.

Compound	Substituent	σ°	$[\sigma^{+}]$	$k/10^{-5}$ s^{-1}
1a	*p*-OMe	−0.27	[−0.70]	16.8
1b	*p*-Me	−0.14	[−0.30]	7.16
1c	H	0		4.44
1d	*p*-Br	0.26		10.6
1e	*m*-NO_2	0.71		6.75
1f	*p*-NO_2	0.81		14.7

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Table 2 Activation parameters of *para*-substituted *N*-methyl-*N*-nitroanilines

Compound	Substituent	% Base[a]	$\Delta V^{\ddagger}$[b]/ml mol^{-1}	$\Delta H^{\ddagger}$[c]/kJ mol^{-1}	$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}
1a	*p*-OMe	1	+18 [376]	159	108
1b	*p*-Me	1	+36 [376]	173	137
1c	H	1	+28 [382]	173	133
1d	*p*-Br	1	+27 [377]	160	106
1e	*m*-NO_2	1	—	148	70
1f	*p*-NO_2	1	+19 [376]	162	113
1f	*p*-NO_2	3	+24 [376]	—	—
1f	*p*-NO_2	5	+32 [376]	—	—

[a] The base is piperidine; concentration is percent by volume. [b] The solvent is toluene; reaction temperature in Kelvins is given in brackets. [c] The solvent is benzene.

Table 3 Product ratios of rearrangement product to parent arylmethylamine of ambient and high pressure reactions. High pressure reactions were conducted at 155 °C for 20 h and *ca.* 1.2 GPa, where solvent free volume is significantly reduced

Substituent	Low pressure	High pressure
p-OMe	0.1	2.5
p-Me	0.1	2.5
H	Trace	1.1
p-Br	Trace	0.3
m-NO_2	Trace	0
p-NO_2	0	0

possible change-over in the reaction mechanism only, and cannot be used alone in elucidating the mechanism. A better survey of the decomposition mechanism was made possible by studying the effect of pressure on reaction rates and product compositions.

Pressure effects

The effect of pressure on reaction rates is an effective means of elucidating the transition state; many examples of interpreting such effects are described in a comprehensive review.[6] For a reaction in solution, the difference in molar volume between the reactant and transition state is defined as the activation volume, $\Delta V^{\ddagger}$. Eqn. (1) gives the isothermal relation between activation volume, rate constant, k, and pressure.

$$\Delta V^{\ddagger} = -RT(\delta \ln k/\delta P)_T \quad (1)$$

The mechanistic features obtained from activation volumes are (*i*) homolytic reactions have positive activation volumes ranging from +5 to +40 ml mol^{-1} and (*ii*) reactions which undergo polarization either by bond formation (*i.e.* the Menshutkin reaction) or bond breaking (*i.e.* heterolysis) have negative activation volumes. At high temperatures, the activation volumes of homolytic reactions are distinctively large owing to the increase in solvent free volume, *e.g.* homolysis of bibenzyl in solution has an activation volume of +31 ml mol^{-1} at 400 °C.[7]

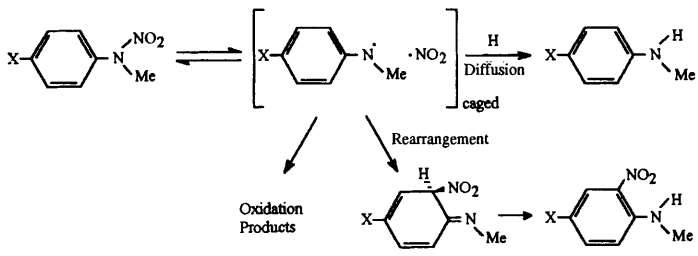
The activation volumes of a series of arylnitramines are given in Table 2 along with their respective activation parameters. In all cases the measured volumes are large positive values and consequently the initial rate-determining step of the reaction cannot be assigned to bond breaking with ionic character, *i.e.* heterolysis of the nitramine bond to the amino cation and nitrite ion. It is proposed that for all arylnitramines the first reaction step is homolysis of the nitramine bond to the arylmethylamino and NO_2 radicals.

The rates of decomposition of compounds **1c** (H) and **1f** (*p*-NO_2) were found to be nearly independent of solvent polarity and is again attributed to a radical mechanism. The observed rate constants (T = 100 °C) for the decomposition of **1f** with 1% by volume piperidine in benzene, acetonitrile and ethanol are 15 × 10^{-5}, 8.4 × 10^{-5} and 17 × 10^{-5} s^{-1}, respectively; the rate constants for decomposition of **1c** with 1% base in benzene and acetonitrile are 4.4 × 10^{-5} and 1.3 × 10^{-5} s^{-1}, respectively. The nitramine, *N*-methyl-*N*-nitro-1-naphthylamine, a compound similar to **1f**, was reported to decompose appreciably faster in acetonitrile than in toluene, and much more so in ethanol.[4] The authors' rate assessments were qualitatively determined by the solution colour change. This aberration is likely to be due to autocatalysis by acid derived from nitrogen oxides and trace water. The addition of piperidine to these decomposition reactions prevents autocatalysis and provides more reliable rate constants.

The correspondingly large $\Delta S^{\ddagger}$ values hold similar mechanistic information as activation volumes. The positive change in $\Delta V^{\ddagger}$ is due to the increase in free space between the solvent molecules and radical pairs generated in the reaction and the positive change in $\Delta S^{\ddagger}$ is due to the increase of translational freedom. Given the low reaction temperatures (*ca.* 100 °C), the reported activation volumes are unusually large when compared with other types of homolytic reactions,[6,8] and those of various alkyl and cycloalkylnitramines were also found to be uncharacteristically large and positive.[3]

The polarity of the nitramine group and reversibility of bond homolysis are two factors that could account for these larger than usual activation volumes. A postulated desolvation effect when a polar nitramine bond dissociates to two less polarized species has been thoroughly discussed.[3] The use of an isotopic scrambling technique and solvent viscosity effect on rates of decomposition of various dialkylnitramines indicated that bond cleavage is reversible.[9] In addition to the evidence, the observed activation volumes of compound **1f** demonstrated a dependence on piperidine concentration; $\Delta V^{\ddagger}$ increases from +19 ml mol^{-1} with 1% piperidine base to +32 ml mol^{-1} with 5% base (Table 2). The activation volume of the thermal decomposition of a ketemine, which undergoes bond dissociation to a caged radical pair, displayed a similar scavenger dependence.[10] In the absence of scavengers, the observed activation volume of pyrolysis of *N*-(1-cyanocyclohexyl)pentamethyleneketenimine is *ca.* +5 ml mol^{-1}. The volume increases to +13 ml mol^{-1} when radical scavengers are in solution, which preclude the reformation of the initiator. Such variability in activation volumes was purported as the effect of pressure on cage reactions in which the observed rate depends on the relative rates of combination and separative diffusion.[8]

The effect of pressure on product yields provided an estimation of relative reaction rates. Solutions of arylnitramines and excess piperidine were infinitely decomposed at ambient and high pressures (*ca.* 1.2 GPa) and analysed for products. The ratio of the rearrangement product to parent arylmethylamine for each nitramine is reported in Table 3. The parent arylmethylamine is derived from the separative diffusion of the caged radical pair. Rearrangement of arylnitramines with electron-donating groups was accelerated by pressure; formation of oxidation products was also found to increase. The reaction of **1a** (*p*-OMe) at ambient pressure gives a small quantity of *p*-methoxyaniline as an oxidation product, but



Scheme 1

$$ArN\dot{}-CH_3 + \cdot NO_2 \longrightarrow HNO_2 + ArN{=}CH_2 \xrightarrow{H_2O} ArNH_2 + CH_2O$$

Scheme 2

increases by a factor of 10 when the decomposition is conducted at 1.3 GPa. Nitramines with electron-deactivating substituents demonstrated no increase in rearrangement nor oxidation. It is clearly evident that secondary cage reactions are greatly assisted by pressure for those arylnitramines having electron-donating substituents.

Mechanism

The proposed mechanism of decomposition for all arylnitramines studied is the reversible homolysis to a caged radical pair, where secondary cage reactions (oxidation and rearrangement) compete with separative diffusion (Scheme 1). The apparent change-over in the Hammett relationship is attributed to an increase in the secondary reactions with electron-donating capability of the substituents.

The proposed route of oxidative demethylation is hydrogen abstraction of the arylmethylamino radical by NO_2 to the corresponding imine and nitrous acid. Hydrolysis of the imine to the parent aniline is effected by trace water generated in the course of decomposition (Scheme 2). The direct formation of the imine from the arylnitramine by elimination of nitrous acid would be accelerated by pressure (negative $\Delta V^{\ddagger}$) and therefore could not be a viable pathway.

Experimental

General procedure

GC–MS was performed with a Hewlett-Packard GC 5890A coupled to a Hewlett-Packard mass selective detector, Model 5970. IR analyses were performed on a Perkin-Elmer FTIR spectrophotometer, Model 1710. UV–VIS spectroscopy was performed on a Milton Roy 1001.

Materials

Compounds **1a**, **1b**, **1c** and **1d** were prepared in a two step process. The potassium salts of *N*-nitroanilines were first prepared by alkaline nitration of the parent anilines with butyl nitrate and potassium ethoxide.[11] These recovered potassium salts were *N*-methylated as described by White *et al.*[12] Nitration of the parent *N*-methylanilines with acetyl nitrate afforded compounds **1e** and **1f**.[13] Identification was made by melting point and all materials had the expected ^1H NMR spectra.

Reactions of arylnitramines

The *N*-methylarylnitramines were decomposed in indifferent solvents, *e.g.* toluene or benzene, to reduce the likelihood of secondary bimolecular reactions between reactant and decomposition products. Nitrogen oxides generated during the course of decomposition react with water and acidify the reaction medium. To hinder catalytic rearrangement by trace acid, a molar excess of an organic base was added to the solutions. The concentrations of base, usually piperidine, ranged from 1 to 5% in volume. In addition to its basic property, piperidine is an efficient scavenger of nitrogen oxides (yielding *N*-nitroso piperidine) and a hydrogen donor. Thermal decompositions of arylnitramine solutions at adiabatic pressures were conducted in sealed glass tubes immersed in a circulated oil bath. The bath temperature was maintained to within ±0.3 °C. All reactions followed first-order kinetics. The rates of decomposition determined from a temperature range of *ca.* 80–120 °C were used to calculate the Arrhenius constants.

Two devices were utilized for reacting arylnitramine solution under high pressures. Activation volumes were measured with a hydraulic apparatus capable of reaching a maximum pressure of 100 MPa. A monoblock cell and hydraulic press were used for decomposing arylnitramine solutions at pressures above 100 MPa. Their construction and procedures have been previously described.[3,14] The activation volumes were calculated from plots of ln *k versus* pressure according to eqn. (1), with pressure in the range 0–100 MPa. Because of the difficulty associated with running reactions under high pressures, the activation volumes have an estimated error of ±5 ml mol^{-1}. The activation volume of compound **1f** was remeasured and found to be lower than the previously reported value.[3] The difference is attributed to a slight modification of the method of analysis and error typical of these measurements.

Analysis

Two spectrometric methods of quantifying the fraction of unreacted arylnitramine were utilized. The rate constants for calculating the activation volumes were measured by following the absorbance of the nitro group's asymmetric stretch by FTIR (*ca.* 1550 cm^{-1}). Solutions were made up such that they had *ca.* 0.7 absorbance units with a NaCl cell having a path length of 0.25 mm. Typical concentrations were of the order of 0.10 M. The ratio of final to initial absorbances, which were adjusted by subtracting the absorbance at infinite decomposition, gave the fraction remaining. The rate constants for determining the Arrhenius parameters were measured by UV–VIS spectrophotometry. Reactant concentrations ranged from 7 to 21 mM and were appropriate for a quartz cell having a path length of 0.1 mm. Because reactant and product spectra overlapped in the region of 275 to 355 nm, reactant concentrations were determined by applying the method developed by Connors and Eboka for two component systems.[15] The molar absorbtion coefficients of unreacted and infinitely reacted solutions for eight to ten wavelengths were used to generate the linear plots.

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