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SHOCK-INITIATION CHEMISTRY OF NITROARENES

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We present evidence that the shock-initiation chemistry of nitroarenes is dominated by the intermolecular hydrogen transfer mechanism discussed previously. The acceleration by pressure, kinetic isotope effect, and product distribution are consistent with the bimolecular transition state rather than rate-determining C-N homolysis. GC-MS analysis of samples which were subjected to a shock wave generated by detonation of nitromethane shows that nitrobenzene produces aniline and biphenyl, and *o*-nitrotoluene forms aniline, toluene, *o*-toluidine and *o*-cresol, but not anthranil, benzoxazinone, or cyanocyclopentadiene. In isotopic labeling experiments *o*-nitrotoluene and TNT show extensive H-D exchange on their methyl groups, and C-N bond rupture is not consistent with the formation of aniline from nitrobenzene or nitrotoluene, nor the formation of *o*-toluidine from *o*-nitrotoluene. Recent work incorporating fast TOF mass spectroscopy of samples shocked and quenched by adiabatic expansion shows that the initial chemical reactions in shocked solid nitroaromatic explosives proceed along this path.

INTRODUCTION

The role of intermolecular reactions in the decomposition of nitroarenes in supercritical aromatic solvents was discussed previously by Minier et al. (1). It was subsequently asserted by Stevenson et al. (2) and Brill and James (3, 4) that C-NO₂ homolysis is the dominant reaction in the shock initiation of nitroarenes, based on the extrapolation of Tsang's (5) gas-phase shock tube Arrhenius plots to high temperatures. Brill and James (4) also state "Almost all studies employ only temperature as the intensive variable. The role of pressure on the rates and mechanisms of reactions of nitroaromatic explosives is essentially unknown."

When the reported pressure and kinetic isotope effects are considered, together with the observed product distributions, it is apparent that

direct C-NO₂ homolysis is not the dominant mechanism in the shock-initiated reactions of nitroaromatic compounds. Decomposition of nitroarenes is known to be strongly accelerated by pressure (1, 6). Minier et al. (1) reported large negative activation volumes, which is inconsistent with the mechanism that Brill proposed.

While rate-determining C-NO₂ homolysis of nitroaromatic compounds is known in the gas phase (5) it has never been documented in condensed-phase experiments. High shock or static pressure reduces the rate of this reaction by a factor of fifty, and accelerates the hydrogen abstraction mechanism by two to three orders of magnitude. We previously stated (6) that the shock-initiation chemistry of nitroarenes is dominated by intermolecular hydrogen atom transfer to the oxygen atom of the nitro group, as discussed previously.

NITROBENZENE

Minier et al. (1) showed that the decomposition of nitrobenzene between 590 and 650 K at 150 to 1360 bar, both neat and in supercritical aromatic solvents, proceeds via formation of a charge transfer complex and hydrogen atom transfer to the oxygen of the nitro group. H-atom transfer lowers the barrier to C-NO₂ homolysis significantly; the observed activation energy for the condensed-phase decomposition of nitrobenzene is less than that for the gas-phase Ar-NO₂ homolysis reaction by 126 kJ/mol. Expulsion of nitrous acid competes with homolysis of the HO-N bond yielding the hydroxyl radical and nitrosobenzene, which is directly reduced to aniline.

The large negative activation volume for nitrobenzene in benzene, $\Delta V^\ddagger = -46 \pm 6$ mL/mol., indicates that bond formation is accompanied by charge separation in the transition state. For nitrobenzene in perdeuterated benzene a primary kinetic isotope effect of 2.5 was found, indicating that abstraction of hydrogen from solvent is the rate-determining step. No isotope effect was found for perdeuterated nitrobenzene in benzene. Substituting toluene as the solvent increases the rate significantly due to the relative ease of abstracting benzylic hydrogen versus aryl.

In the shock recovery experiments discussed previously (6-8) nitrobenzene was decomposed by a shock generated by detonation of nitromethane. Decomposition of nitrobenzene in benzene, cyclohexane or toluene solvents produces aniline as well as benzene. Isotopic labeling shows that the original C-N bond is preserved in the product aniline. The observed rate is consistent with the Arrhenius parameters and pressure effect measured previously for the condensed-phase reduction. Aniline formation, discussed in detail by Minier, is inconsistent with decomposition via direct Ar-NO₂ homolysis.

o-NITROTOLUENE

Decomposition of *o*-nitrotoluene also proceeds via intermolecular hydrogen abstraction,

although a competitive intramolecular cyclization reaction, leading to the formation of anthranil and its subsequent decomposition products, was also discussed by Minier et al. (1) and previous researchers noted therein. An analogous mechanism has been proposed by Sharma et al. for the thermal decomposition of TATB (9). For *o*-nitrotoluene in perdeuterated benzene a primary kinetic isotope effect of 1.7 was measured. Anthranilic acid, aniline, *o*-aminobenzaldehyde, benzoxazinone, and benzoylene indazole are minor products characteristic of the intramolecular cyclization reaction, although aniline may also result from oxidation of the methyl group of *o*-toluidine followed by decarboxylation. Stevenson et al. (2) raise the possibility that anthranil undergoes a ring-contraction reaction to cyanocyclopentadiene.

In shock recovery experiments using benzene solvent, the dominant product is *o*-toluidine; no other toluidine isomers are observed. Toluene and aniline are found as well, along with biphenyl. There are no detectable amounts of the products diagnostic of the intramolecular cyclization reaction; and no cyanocyclopentadiene is observed. In our shock recovery experiments there is a primary deuterium kinetic isotope effect of 1.5, which compares favorably with the value of 1.7 for the static experiments.

Shock-induced decomposition of *o*-nitrotoluene in perdeuterated benzene solvent reveals that all of the products listed above and the starting material show H-D exchange, and the biphenyl is perdeuterated which indicates it is formed from coupling of phenyl radicals. Toluene formed in these experiments has incorporated one or two deuterium atoms, indicating that it is formed from *o*-nitrotoluene instead of methylation of benzene; and this is also true of the aniline. *O*-toluidine shows some H-D exchange but is predominantly protic, which indicates that it originated directly from the starting material by reduction of the nitro group. All of these observations support the mechanism proposed by Minier et al. (1).

Figure 1 shows some of the results obtained from GC-MS analysis of a shock-recovery experiment performed on *o*-nitrotoluene in

perdeuterated benzene; a small quantity of β -pinene is also present as an internal thermometric standard. (8) This sample was confined in a steel capsule and shocked by detonation of nitromethane with 10% acetone and 2.5% DETA; the extent of reaction was 56%. Mass spectra are shown for the products with mechanistic significance.

FIGURE 1. GC-MS analysis of shock-induced reaction of *o*-nitrotoluene in perdeuterated benzene, showing isotope distributions in the mass spectra of selected products. Top is total ion chromatogram, followed by mass spectra for toluene, aniline, *o*-toluidine, unreacted *o*-nitrotoluene, and perdeuterated biphenyl. All compounds have been positively identified and are consistent with Minier's mechanism.

TATB AND TNT

Time-of-flight mass spectral data for the shock-induced decomposition of TATB (1,3,5-

triamino-2,4,6-trinitrobenzene) has been discussed previously. (10-12) This data was obtained with a unique collisionless mass spectrometer, designed and built specifically for studying the shock initiation chemistry of explosives, which is described elsewhere. (13-15) Thorough calibration of the electric slappers using VISAR has been performed by Engelke and Blais. (16) The shock delivered to the samples is well-characterized; the reactive intermediates are expanded adiabatically into a hard vacuum and sampled via a molecular beam formed from a central region of the expansion fan, where compression and decompression is effectively uniaxial.

By comparing mass spectra recorded at different input stresses and examining the number of counts as a function of time for different peaks Östmark (12) showed that a mass peak at $m/z = 242$ is an authentic reaction product from the shock-induced decomposition of TATB, and not an artifact of the electron gun, nor present in the cracking pattern of unreacted TATB. Through deuterium and nitrogen-15 isotopic labeling, Greiner et al. (10) and Östmark (12) also demonstrated that this corresponds to loss of oxygen, and not NH_2 , from the parent molecule. As in the simpler nitroaromatic compounds, direct reduction of nitro- to nitroso- is consistent with the intermolecular hydrogen atom transfer mechanism discussed previously. In the (unlabeled) TATB spectra reported previously (10) there is also a peak at $m/z = 228$, or 30 mass units lighter than the starting material. Greiner et al. identified this as loss of NO from the parent molecule. We attribute this to hydrogen atom transfer followed by C-N fission, rearrangement and recombination, and subsequently loss of nitroxyl as discussed previously. (1)

Shackelford (17-19) and Rogers, Janney, and Ebinger (20) have previously documented a primary deuterium kinetic isotope effect (DKIE) in the decomposition of TATB, TNT, and other solid explosives. They clearly state that homolytic C-H bond rupture must be the rate controlling step in the decomposition of these compounds, and Shackelford cites additional

evidence obtained via electron paramagnetic resonance (EPR) spectroscopy.

Figure 2 shows a high-mass scan (near the mass of parent molecule) from the detonation mass spectrometer studies of TNT reported previously. (10) It is apparent that, as with TATB, loss of oxygen from the parent molecule dominates the process and any contribution from C-N homolysis ($m/z=181$) is negligible.

Figure 2. Scan 20 from detonation mass spectrometer study of TNT. Note that a mass peak at $m/z=228$ is recorded while the mass of TNT is 227. Ratio of relative intensities for peaks at $m/z=211$ to the starting material parent ion changes significantly with time, indicating that $m/z=211$ is due to formation of a reaction product and not just the cracking pattern of TNT.

CONCLUSION

There is a significant body of evidence supporting the contention that shock-induced reaction in nitroaromatic compounds proceeds through intermolecular hydrogen abstraction. In shock recovery experiments on nitrobenzene, *o*-nitrotoluene, and TNT we observe a primary DKIE and isotopic scrambling on methyl substituents. Product distribution is consistent with the hydrogen abstraction mechanism and not rate-determining C-N homolysis. Results of studies performed on solid nitroaromatic explosives with the LANL detonation mass spectrometer are consistent with this mechanism.

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