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Role of Intermolecular Reactions in Thermolysis of Aromatic Nitro Compounds in Supercritical Aromatic Solvents

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Several nitroarenes were decomposed isothermally in dilute supercritical solution in benzene or toluene and in the vapor phase in the temperature range of 290–380 °C in sealed glass tubes with pressures up to 100 MPa. The mechanisms of thermolysis are inferred from kinetic studies and product analysis. The initial rate-controlling step for nitrobenzene and *p*-nitrotoluene decomposition is probably intermolecular hydrogen abstraction to form an $ArNO_2H$ radical intermediate. The nature of the transition state is deduced from the activation volume (ΔV^*), H/D kinetic-isotope effect, and a linear free-energy relationship between the ionization potential of the hydrogen donor and the logarithm of the decomposition rate. A concurrent pathway for *o*-nitrotoluene is an intramolecular reaction in which anthranil is an intermediate. The behavior of 1,3-dinitrobenzene and 1,4-dinitrobenzene resembles that of nitrobenzene, whereas 2,4-dinitrotoluene and 2,6-dinitrotoluene decompose in the same manner as *o*-nitrotoluene. Activation parameters are given and detailed mechanisms proposed.

Introduction

The subject of this paper is the thermal decomposition of nitrobenzene, *o*-nitrotoluene, *p*-nitrotoluene, dinitrobenzenes, and dinitrotoluenes in aromatic solvents from 290 to 380 °C. Nitroarene thermolyses were conducted in supercritical benzene or toluene. This approach offered several advantages: the density-dependent properties of the medium could be controlled by the pressure, bimolecular reactions of the solute with itself or its degradation products were minimized, and pathways involving reactive radicals were clarified by identification of products derived from the scavenging action of the solvent.

Studies of nitrobenzene vapor at ordinary pressure have shown that $C-NO_2$ homolysis is an important initial process. Activation energies (E_a) range from 214 to 292 kJ/mol.[1-12] Gaseous 1,3-dinitrobenzene and 1,4-dinitrobenzene have also been reported to decompose initially by $C-NO_2$ homolysis with E_a values between 221 and 283 kJ/mol.[7,10,13,14] *p*-Nitrotoluene has been reported to decompose by $C-NO_2$ cleavage and by $C-NO_2$ isomerization with E_a values between 257 and 283 kJ/mol.[7,10,12,15] For *o*-nitrotoluene thermolysis, unique products, faster decomposition rates, and low E_a values (178–215 kJ/mol) have led to proposed intramolecular mechanisms,[3,6,15,16] possibly forming anthranil as an intermediate,[17] although $C-NO_2$ cleavage has also been proposed.[10,18] An EPR study of liquid *o*-nitrotoluene decomposition suggested transfer of a hydrogen atom to produce an $Ar-NO_2H$ radical.[19] Both 2,4-dinitrotoluene and 2,6-dinitrotoluene vapors have been reported to decompose intramolecularly[8,20] or by $C-NO_2$ homolysis.[9,10,17]

We show that the initial decomposition step for nitrobenzene and the dinitrobenzenes in dense supercritical benzene is hydrogen abstraction from solvent, whereas *o*-nitrotoluene and the dinitrotoluenes decompose primarily through an intramolecular pathway involving an anthranil intermediate.

Experimental Section

Thermolyses. Nitroarenes and solvents were obtained from either Aldrich or Fluka Chemical Co. and were used as received. Solutions of 4–10% nitroarene in solvent (typically benzene or toluene) were isothermally decomposed in sealed glass capillary tubes (40–50-μL total volume), filled, and heat-sealed to 50–60% capacity. Vapor decomposition was conducted on 1.0 μL of neat nitroarene, in an inert environment, in a heat-sealed 500-μL glass bulb. The isothermal bath apparatus consisted of an aluminum block bored to accommodate wells for the following: a 10-cm deep × 2.5-cm wide well for molten metal, an immersion heater, a temperature controller, and a resistance thermometer. A hot plate acted as a base heater for the aluminum block. A 36 × 91 cm two-ply Plexiglas safety shield was placed in front of the apparatus. Lead and/or Wood's metal was used as the bath metal. The bath apparatus maintained a constant temperature within 1 °C for the temperature range of the study (290–380 °C). A majority of the sealed capillary tubes was capable of containing up to 100 atm during thermolysis without bursting. Small scale and shielding prevented possible harm from any ruptured tubes.

For high-pressure thermolyses, the tubes were placed in a high-pressure reactor that could be inserted into a preheated aluminum block. The reactor consisted of a length of 0.6-cm stainless steel capillary tubing with one end welded closed.[21] Up to 1400 atm of external pressure could be safely applied into the reactor without imploding the capillary tube. The time constant of this apparatus was approximately 60 s. Immediate observation

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Table I. Thermolysis Products from 10% Nitrobenzene in Benzene at 343 °C (44% Reacted)[a]

rel conc[b]	products
	water[c]
10.3	aniline
5.3	phenol
100.0	biphenyl
11.4	*N*-phenylaniline
24.0	1,1′:2′,1″-terphenyl
7.8	1,1′:3′,1″-
3.9	*o*-nitrobiphenyl
3.4	*m*-
14.2	*p*-
14.0	azobenzene

[a] Capillary tubes ~60% filled, identification by GC-MS. [b] Normalized to biphenyl. [c] Detected but not quantified.

of a tube removed from the bath or reactor showed the reaction mixture to be homogenous.

The pressure generated inside a capillary tube by the supercritical fluid was set in advance by use of a method developed by Brower[22] where the pressure generated at a specific temperature was determined as a function of benzene density with use of PVT data.[23] Pressure contributions from the nitroarenes were assumed to be negligible because of their low concentration. The internal pressure was increased by increasing the fractional filling of the nitroarene solution in the capillary tube.

Product Analysis. The composition of the reaction mixture was determined by GC-MS. A universal sensitivity factor was applied since peak intensities were within 15% of each other for standardized solutions containing equimolar amounts of typical products found in this study. The relative peak intensities of products were calculated by setting the abundant ion at 100%.

Rate Constants. A pseudo-first-order rate law gave a good fit to the data, although the rate is probably first order in solvent also.

$$(-d[ArNO_2]/dt) = k'[ArNO_2][\text{solvent}] \qquad (1)$$

where $[ArNO_2]$ is the nitroarene concentration and k' is the second-order rate constant.

The fraction of unreacted nitroarene was quantified by use of solvent as an internal standard. External standards were used for vapor-phase studies. Rates were measured from 290 to 380 °C. A temperature of 343 °C was arbitrarily chosen for comparison of rate effects caused by variation of structure, isotopic composition, and other factors.

Results and Discussion

Nitrobenzene. Nitrobenzene vapor at 343 °C and 150 atm showed very little reaction after 15 h. The rate constant, approximately 10^{-7} s^{-1}, is ~100 times greater than the rate constants extrapolated from literature for C–NO_2 homolysis. There may have been an initiating step faster than C–NO_2 homolysis, or the surface may have catalyzed decomposition. The only product identified was a trace of benzene and a light brown, insoluble film, probably derived from radicals produced during thermolysis. The formation of benzene is probably due to hydrogen abstraction by a phenyl radical.

Nitrobenzene thermolysis at 343 °C in supercritical benzene,[24,25] 150 atm and 0.44 g/mL, was studied in great detail. The major products and their peak intensities are listed in Table I.[26] The rate constant, 1.0×10^{-4} s^{-1}, is at least 1000 times greater than for vapor thermolysis at 343 °C. The E_a found for solution thermolyses between 320 and 380 °C, 166.3 kJ/mol, was ~126 kJ/mol less than the E_a reported for C–NO_2 bond homolysis. The rate law for nitrobenzene in benzene was

$$k(\text{nitrobenzene}) = 1.3 \times 10^{10} \exp(-20\,051/T)\ s^{-1}\ {}^{26}$$

With thermolysis in benzene-d_6, a primary KIE of 2.5 was found and most of the biphenyl was fully deuterated. This suggests that a transfer of hydrogen from benzene to nitrobenzene (1) was involved in the rate-limiting step to produce a $C_6H_5NO_2H$ radical (4) and a phenyl radical (5) (Scheme I). Hydrogen was predominantly abstracted from solvent molecules as no KIE was found with nitrobenzene-d_5 thermolysis. Such molecule-induced hydrogen abstraction homolyses have been reported in the literature.[27-32]

A pressure effect on the rate constant was found in the interval from 152 to 1172 atm at 320 °C. A plot of the natural logarithm of the rate constant versus pressure (eq 2) gave a value of −46 ± 6 mL/mol for ΔV^* between 200 and 750 atm. The negative value shows that the reaction

$$(\delta \ln k/\delta P)_T = -\Delta V^*/RT \qquad (2)$$

is characterized by a decrease in molar volume in the transition state. This is typical of bond-forming processes and in agreement with previous observations on hydrogen abstraction.[33-35] The unexpected large magnitude of ΔV^* could be explained by an electrostriction effect resulting from a polarized transition state. Such a state would form if the electron and hydrogen nucleus were not transferred simultaneously, resulting in a charge-transfer type of intermediate. It is well-known that nitrobenzenes are good electron acceptors[36-39] and benzene and substituted benzenes are good π electron donors in charge-transfer complexes.[40]

The formation of a charge-transfer type transition state is supported by the existence of a linear free-energy relationship (LFER) between the ionization potential (IP) of monosubstituted benzene solvents and the logarithm of the thermolysis rate constant. The rate constant was decreased by electron-withdrawing and increased by electron-donating substituents.[26] Product analyses indicated that arylation by solvent-derived radicals occurred in each case in the same way that biphenyl is formed by nitrobenzene in benzene. The LFER was well obeyed except for *N*,*N*-dimethylaniline; the methyl hydrogens were abstracted as well as the ring hydrogens, resulting in faster nitrobenzene thermolysis. This was not observed for anisole. Interestingly, neat liquid nitrobenzene acted as its own donor and fit the LFER well.

The dominant fates of the reaction intermediates are presented in Scheme I. Most of the phenyl radicals arylate

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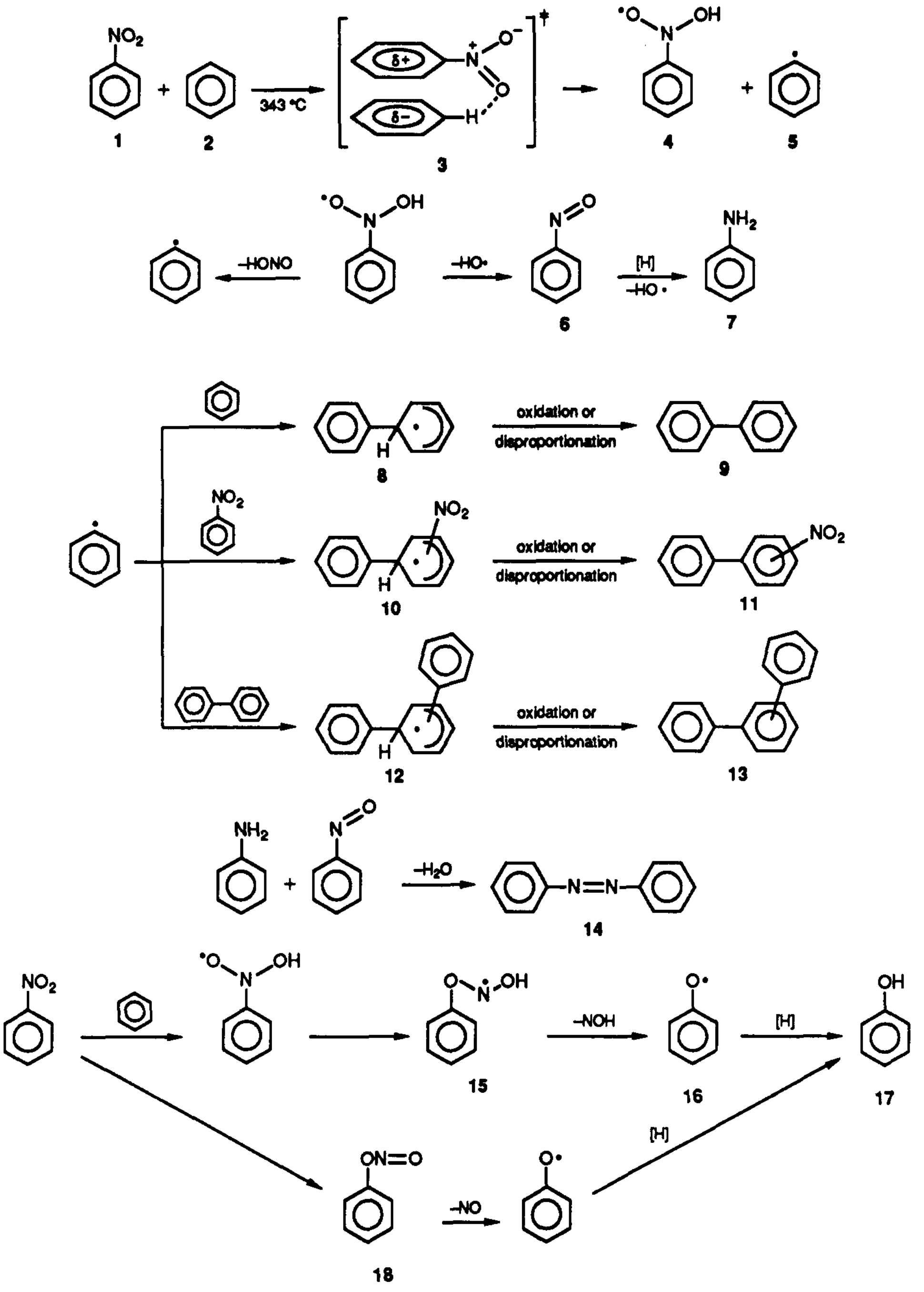
Scheme I. Nitrobenzene Decomposition Mechanism in Supercritical Benzene



solvent molecules to produce biphenyl (9).[3,4,32] Continuation of the phenylation reaction yields terphenyl (13) and the nitrobiphenyl isomers 11. In solution, nitrobenzene is said to be preferentially arylated by radicals in the ortho and para positions.[41] The electronic meta-directing influence of the nitro group in electrophilic reactions did not appear to have a strong influence in this study. The absence of a KIE when nitrobenzene-d_5 was thermolyzed in supercritical benzene suggests that hydrogen abstraction from nitrobenzene to form a nitrophenyl radical is not a favored decomposition path.

The $C_6H_6NO_2H$ radical decomposed by two pathways (Scheme I): it was reduced to aniline (7), or homolysis of the $C_6H_6NO_2H$ bond occurred to yield a phenyl radical (5) and HONO. In the formation of aniline, nitrosobenzene (6) is the hypothesized intermediate.[42] Since nitrosobenzene is electropositive relative to nitrobenzene, it was reduced too quickly for detection, especially under the severe conditions of this study. The presence of nitrosobenzene was supported by the detection of the thermolysis product azobenzene (14), the condensation product of nitrosobenzene and aniline.[43] In a separate experiment, an equimolar mixture of aniline and nitrosobenzene in benzene at 343 °C yielded azobenzene.

Evidence for C_6H_5–NO_2H bond homolysis was found in the thermolysis products from the nitrobenzene/benzene-d_6 system where biphenyl-d_5 was formed. Selected-ion analysis for perdeuterated biphenyl and for biphenyl-d_5 indicated that ~20% of the biphenyl contained a phenyl

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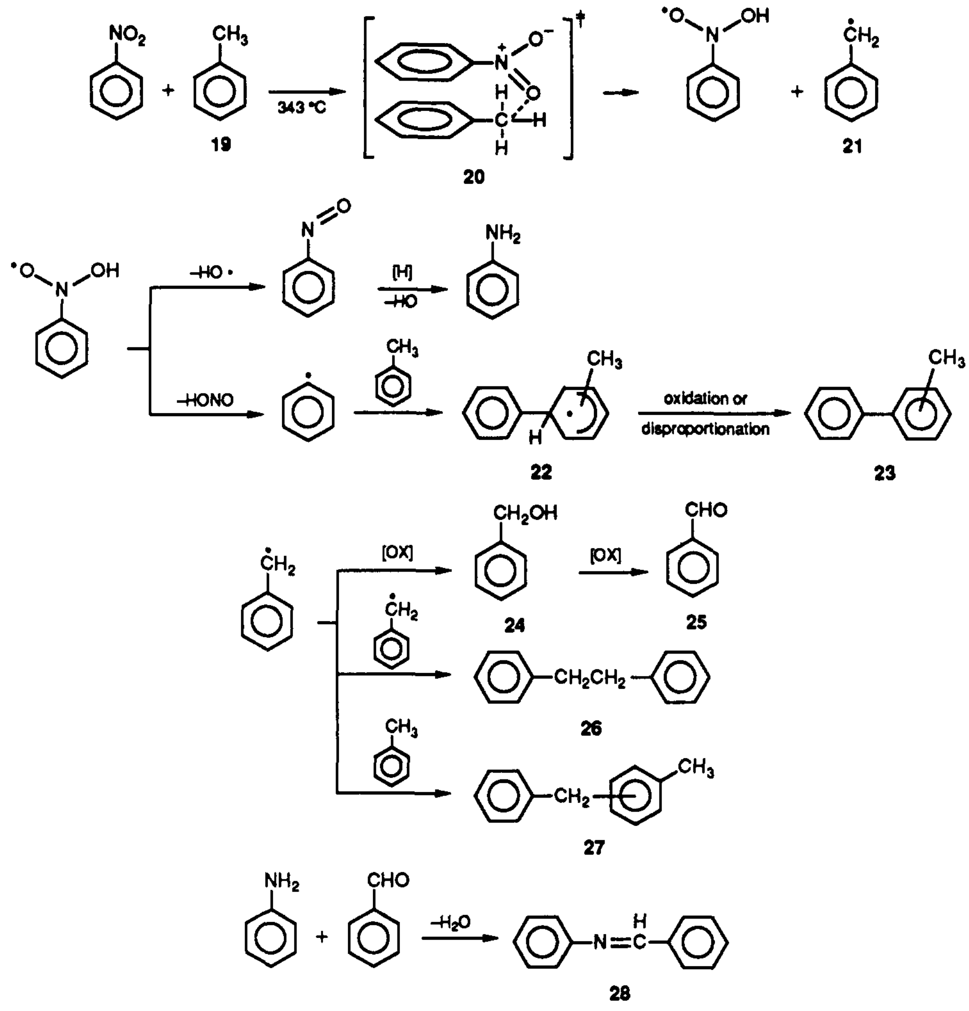
Scheme II. Nitrobenzene Decomposition Mechanism in Supercritical Toluene



ring from nitrobenzene. Likewise, in the nitrobenzene-d_5/benzene-thermolyzed system, ~25% of the biphenyl contained a phenyl ring derived from nitrobenzene-d_5.

Phenol (17), a minor thermolysis product, has been reported in other nitrobenzene thermal studies.[4,44-46] Phenol may have been derived from a nitro–nitrite rearrangement since phenol-d_5 was produced in the nitrobenzene-d_5/benzene thermolysis. Another possible source of phenol is the oxidation of the phenyl radical produced in C–NO_2H homolysis by the HONO trapped in the solvent cage (Scheme I).

Nitrobenzene Thermolysis in Supercritical Toluene. Nitrobenzene thermolysis in supercritical toluene,[25] having a density of ~0.43 g/mL, was studied in detail from 320 to 380 °C. Toluene was used as a solvent because both benzylic and aromatic hydrogens were available for abstraction. Thermolysis products are listed in Table II. The products derived from nitrobenzene suggest that the reaction paths (Scheme II) are similar to those for nitrobenzene in supercritical benzene. The toluene-derived products show that nitrobenzene preferentially abstracts the benzylic hydrogen from toluene, forming the $C_6H_5NO_2H$ radical and benzyl radical (21) along with a small amount of methylphenyl radicals. The benzyl radical is oxidized to benzyl alcohol (24) and benzaldehyde (25). The toluene-derived products indicate that benzylic hydrogens are abstracted in preference to nuclear hydrogens. Indisputable evidence for the intermediacy of benzyl radicals is the formation of bibenzyl (26). A primary KIE of 3.5 in toluene-d_8 supports the concept of rate limitation by hydrogen abstraction.

Table II. Thermolysis Products from 4% Nitrobenzene in Toluene at 343 °C (85% Reacted)[a]

rel conc[b]	products
3.3	benzaldehyde
100.0	aniline
14.1	*o*-methylbiphenyl
6.9	*p*-
5.9	bibenzyl
57.9	*N*-(phenylmethylene)benzenamine
20.3	benzyl alcohol

[a] Capillary tubes approximately 60% filled, identification by GC–MS. [b] Normalized to aniline.

The rate constant for nitrobenzene in toluene at 343 °C, 6.3×10^{-4} s^{-1}, was more than 6 times the rate constant for nitrobenzene in benzene. A higher rate in toluene was expected because the bond strengths of the aromatic and benzylic C–H bonds, 464 and 368 kJ/mol, respectively,[47] make benzylic hydrogens more susceptible to abstraction than aromatic hydrogens. However, the rate difference was not as large as expected, probably due to the effect the solvent IP has on the formation of the transition state complex. The reported solvent IP's are 9.1[48] and 8.9 eV[49]

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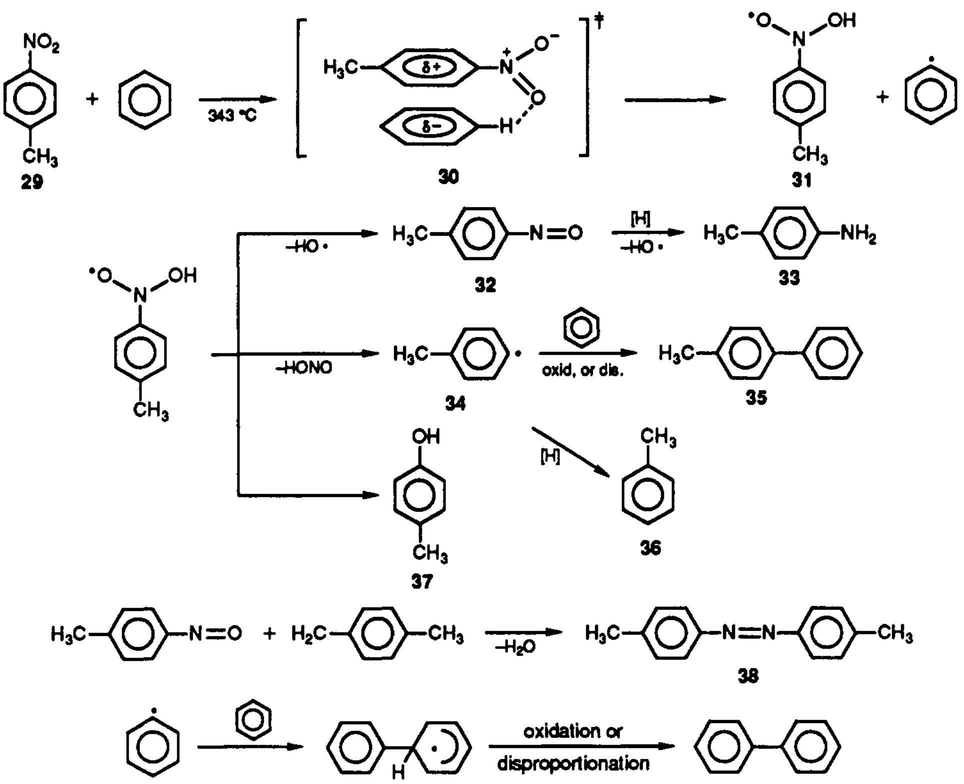
Scheme III. *p*-Nitrotoluene Decomposition Mechanism in Supercritical Benzene



for toluene and 9.4 eV[49] for benzene. The similarity in IP may explain why the rate constant in toluene was greater than in benzene only by a factor of 6.

The principal fates of the reaction intermediates are shown in Scheme II. Further reaction of the $C_6H_5NO_2H$ radical in toluene follows two major routes just as it does in benzene: homolysis and concurrent reduction. Evidence for $C{-}NO_2H$ homolysis was the detection of methylbiphenyl isomers **27**. About 20% of the nitrobenzene reacted in this way. The remainder was reduced to aniline. Azobenzene was not observed in the products. In toluene, nitrosobenzene is apparently reduced faster than it can condense with aniline. This is not surprising since toluene is a better reducing agent than benzene. Condensation of aniline with benzaldehyde yielded *N*-(phenylmethylene)benzenamine (**28**).[43]

***p*-Nitrotoluene Thermolysis in Supercritical Benzene.** The thermolysis of *p*-nitrotoluene (**29**) in benzene at 343 °C yielded products structurally analogous to those found in the nitrobenzene/benzene thermolyses (Table III). The rate constants for *p*-nitrotoluene and nitrobenzene in supercritical benzene were the same, 1.0 × 10^{-4} s^{-1}. The presence of the electron-donating methyl substituent apparently had little effect upon the decomposition rate. The E_a and log Z for *p*-nitrotoluene in benzene from 333 to 380 °C were comparable to the kinetic parameters obtained for nitrobenzene in benzene. The rate law is

$$k(p\text{-nitrotoluene}) = 7.9 \times 10^9 \exp(-19596/T)\ \mathrm{s}^{-1}$$

The similarity of rate constants, kinetic parameters, and products implied a decomposition mechanism similar to that of nitrobenzene. A primary KIE of 1.8 for *p*-nitrotoluene in benzene-d_6 supported hydrogen abstraction from benzene as the rate-limiting step. Furthermore, anisole and chlorobenzene showed a substituent effect with *p*-nitrotoluene as had been found for nitrobenzene. The major decomposition channels proposed for *p*-nitrotoluene thermolysis are presented Scheme III.

Table III. Thermolysis Products from 4% *p*-Nitrotoluene in Benzene and Toluene at 343 °C (38 and 90% Reacted, Respectively)[a]

rel conc[b]	products
	in Benzene
2.2	toluene
20.3	*p*-toluidene
4.7	*p*-cresol
100.0	biphenyl
19.8	4-methylbiphenyl
0.8	4,4′-dimethylazobenzene
	in Toluene
29.7	benzaldehyde
100.0	benzyl alcohol
37.4	*p*-toluidene
4.3	*p*-methylbiphenyl
17.2	toluene dimers
4.4	bibenzyl
49.2	*N*-benzylidene-4-methylaniline

[a] Capillary tubes ~60% filled, identification by GC-MS. [b] Normalized to biphenyl for benzene and to benzyl alcohol for toluene.

***p*-Nitrotoluene Thermolysis in Supercritical Toluene.** Similar intermolecular mechanisms, reduction and condensation, appear to be operating for *p*-nitrotoluene in toluene as for nitrobenzene in toluene. Toluene acts as a reducing agent, with benzylic hydrogens abstracted in preference to aromatic hydrogens. The chief reduction product is *p*-toluidine (**40**) (Table III). The hypothetical pathways for *p*-nitrotoluene in supercritical toluene, based upon the observed thermolysis products, are summarized in Scheme IV.

***o*-Nitrotoluene Vapor Thermolysis.** The rate constant for *o*-nitrotoluene (**41**) vapor at 343 °C is 3.6 ± 1.3

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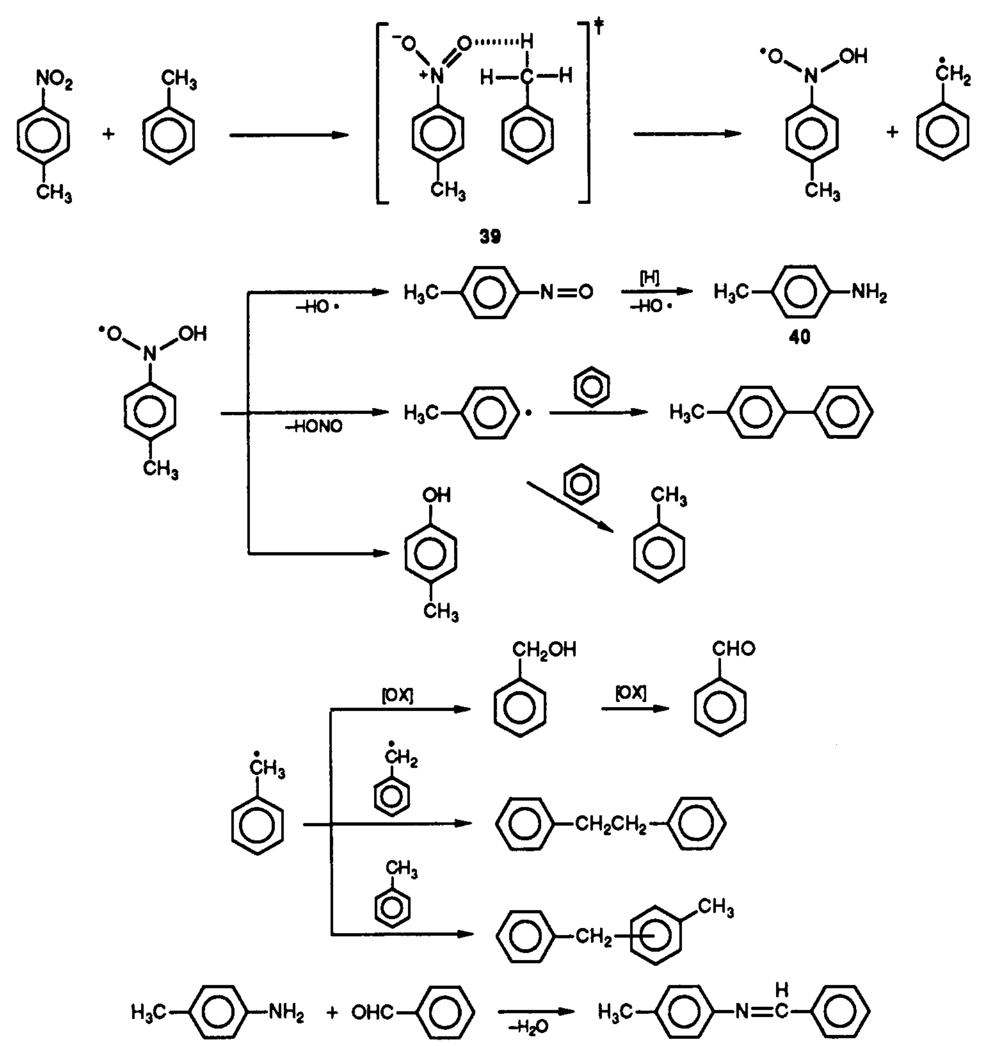
Scheme IV. *p*-Nitrotoluene Decomposition Mechanism in Supercritical Toluene



$\times 10^{-5}$ s^{-1}, which is 3–7 times greater than previously reported values[7,8,15] and roughly 400 times greater than the values reported for C–N bond homolysis at low concentrations.[10,12] When neat o-$CD_3C_6H_4NO_2$ was thermolyzed, a primary KIE of 1.7 was found.

A polymeric brown film formed on the surface of the reaction bulb. Among the monomeric products were aniline and a compound with a parent peak of m/e 210, possibly 2-phenylindazol-3-one.[50] The use of 300-μL ampules instead of 500-μL ampules produced trace amounts of o-aminobenzaldehyde and o-toluidine. The presence of o-toluidine is evidence that bimolecular reduction occurred during thermolysis. The nitro group is probably reduced by a mechanism similar to that described for the formation of aniline from nitrobenzene. It has been proposed that gaseous o-nitrotoluene rearranges to anthranilic acid by "the formation of a carbanion species followed by a series of hydrogen and oxygen shifts."[8,20] Decarboxylation of the acid yields aniline. In a separate experiment, gaseous anthranilic acid at 343 °C for 11 min yielded 72% aniline. Both the formation of aniline and the primary KIE are consistent with this mechanism. However, there is some skepticism about this gaseous rearrangement.[10,17] Tsang et al.[17] "deduced a mechanism which at lower temperatures is probably the sole channel for the decomposition of any nitroaromatic compound with an adjacent methyl grouping" involving the intermediate anthranil (3,4-benzisoxazole). Anthranil appears to be a key intermediate in this study.

Table IV. Thermolysis Products from *o*-Nitrotoluene in Benzene at 343 °C (35% Reacted)[a]

rel conc[b]	products
	water[c]
11.0	aniline
1.5	o-cresol
4.3	o-toluidene
60.9	o-aminobenzaldehyde
100.0	biphenyl
31.5	o-anthranilic acid
2.6	2-nitrodiphenylmethane
1.8	x-phenyl-o-nitrotoluene
3.7	o-methylbiphenyl
2.6	2,2′-dimethylazobenzene
15.1	benzoyleneindazole
27.5	benzoxazinone

[a] Capillary tubes ~60% filled, identification by GC–MS. [b] Normalized to biphenyl. [c] Detected but not quantified.

***o*-Nitrotoluene Thermolysis in Supercritical Benzene.** Thermolysis of 4–10% o-nitrotoluene in supercritical benzene at 343 °C gave the products listed in Table IV. The products structurally related to those from the thermolysis of p-nitrotoluene were biphenyl, o-toluidine (50), o-cresol (43), and o-methylbiphenyl (51) (Scheme V). A primary KIE of 1.7 was found for thermolysis in benzene-d_6, providing evidence of the intermolecular reactions described for p-nitrotoluene and ni-

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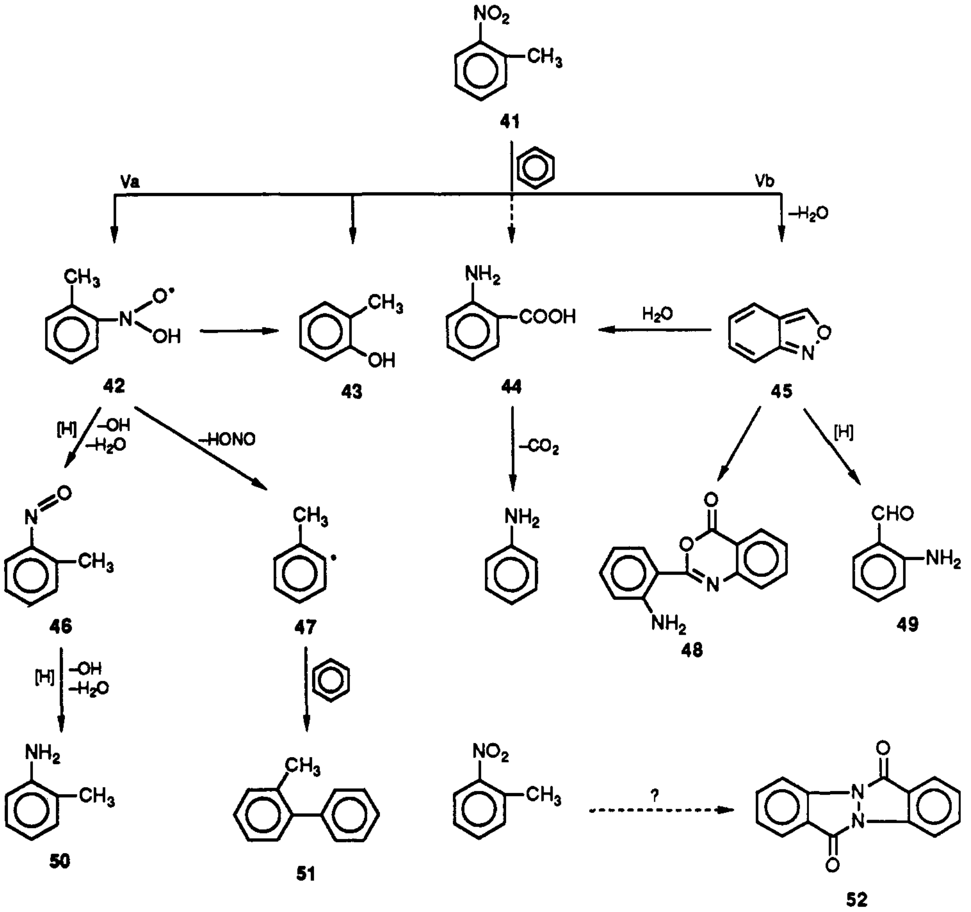
Scheme V. *o*-Nitrotoluene Decomposition Mechanism in Supercritical Benzene



trobenzene. Products unique to *o*-nitrotoluene were aniline, anthranilic acid (**44**), *o*-aminobenzaldehyde (**49**), benzoxazinone (**48**), and benzoylene indazole (**53**). Their formation is attributed to intramolecular reactions of the adjacent methyl and nitro substituents. A primary KIE of 1.9 was found for *o*-$CD_3C_6H_4NO_2$ in benzene, supporting intramolecular reactions.

The rate constant for *o*-nitrotoluene thermolysis at 343 °C, $1.4 \pm 1.1 \times 10^{-3}\ \mathrm{s}^{-1}$, was ~14 times greater than those of nitrobenzene and *p*-nitrotoluene under similar conditions. The increase in rate must be due to the availability of intramolecular reaction channels in addition to the previously discussed intermolecular pathways. The E_a, 159.3 kJ/mol, is similar to those found for nitrobenzene and *p*-nitrotoluene. The rate law is described by

$$k(o\text{-nitrotoluene}) = 5.0 \times 10^{10} \exp(-19242/T)\ \mathrm{s}^{-1}$$

Intermolecular Decomposition of *o*-Nitrotoluene. The thermolysis products biphenyl, *o*-toluidine (**50**), and *o*-methylbiphenyl (**51**) and the solvent primary KIE of 1.7 are indicative of the same intermolecular hydrogen abstraction mechanism occurring as has been proposed for nitrobenzene and *p*-nitrotoluene (Scheme Va). After the rate-limiting step, *o*-nitrotoluene is reduced to *o*-nitrosotoluene (**46**). The instability of *o*-nitrosotoluene at 343 °C was confirmed when a 15% solution of *o*-nitrosotoluene was thermolyzed in benzene at 250 °C for 2 h and none remained. The main thermolysis products were *o*-toluidine, *o*-nitrotoluene, *o*-aminobenzaldehyde, *o*-methylbiphenyl, and biphenyl, all of which were also detected in o-nitrotoluene thermolysis.

The $ArNO_2H$ radical (**42**) can react to yield *o*-nitrosotoluene or a 2-methylphenyl radical (**47**). *o*-Nitrosotoluene is reduced to *o*-toluidine, and the 2-methylphenyl radical subsequently arylates a benzene molecule to form 2-methylbiphenyl (Scheme Va). Hydrogen abstraction by the 2-methylphenyl radical to form toluene apparently did not occur since toluene was not detected. There was a 1:1 ratio of *o*-toluidine (**50**) to *o*-methylbiphenyl (**51**), indicating equal probabilities for either route.

The identification of 2-nitrodiphenylmethane (Table IV) reveals that the benzylic hydrogens of *o*-nitrotoluene are abstracted. The resulting nitrobenzyl radical (O_2N-$ArCH_2^{\bullet}$) adds to benzene to yield the product. This mechanism has been proposed as the rate-limiting step in thermolysis of neat TNT at 240 °C.[51] Discussion of other minor intermolecular pathways for *o*-nitrotoluene may be found in ref 26.

Intramolecular Decomposition of *o*-Nitrotoluene. The possible involvement of anthranil (**45**) as an intermediate in *o*-nitrotoluene thermolysis was suspected. We have found that a 10% solution of anthranil in benzene, heated to 343 °C for 40 s, produced gas, a black tar, and 30% benzoxazinone. Biphenyl was not detected in the products, indicating hydrogen abstraction from solvent was not involved. Benzoxazinone was separated, purified, and identified. It has been proposed that benzoxazinone is derived from the cycloaddition of a ketene–imine intermediate that is a valence tautomer of benzoazetidone.[52,53] In the reaction conditions of this study, this type of reaction may be occurring. However, the intermediate may also form by a retroarene reaction which has been proposed by Tsang et al.[17]

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Table V. Thermolysis Products from 4% *o*-Nitrotoluene in Toluene at 343 °C (33% Reacted)[a]

rel conc[b]	products
21.3	aminobenzaldehyde
6.2	benzaldehyde
trace	aniline
100.0	benzyl alcohol
22.2	*o*-toluidene
4.0	toluene dimers (6)
1.6	bibenzyl
5.6	aminobibenzyl, *x*-amino-*x*′-diphenylmethane
9.0	*N*-benzylidene-2-methylaniline

[a] Capillary tubes ~60% filled, identification by GC–MS. [b] Normalized to benzyl alcohol.

Anthranil appears to be the intermediate in formation of *o*-aminobenzaldehyde. At first it was suspected that *o*-nitrosotoluene underwent a 1,5-sigmatropic rearrangement to *o*-aminobenzaldehyde. However, this rearrangement can be discounted due to the increase in rate constant observed for *o*-nitrotoluene relative to *p*-nitrotoluene; the reduction of the nitro group to nitroso would not be accelerated by an adjacent methyl group. When 10% anthranil was thermolyzed in toluene at 343 °C, the products were 90% benzoxazinone and 10% *o*-aminobenzaldehyde. As the concentration of anthranil in toluene was decreased to 1% to suppress dimerization, *o*-aminobenzaldehyde became the major product, supporting anthranil as the intermediate (Scheme Vb).

Anthranil has been proposed as an intermediate in the formation of anthranilic acid from *o*-nitrotoluene[8,20,54-57] and this study supports that proposal. Thermolysis of 20 μL of anthranil and 1 μL of water in supercritical benzene yielded the acid, aniline, and benzoylene indazole. Thermolysis of only the acid in supercritical benzene yielded only aniline. Apparently, anthranil is converted to the acid, which decarboxylates to yield aniline.

The evidence suggests anthranil to be the key intermediate for the formation of benzoxazinone, *o*-aminobenzaldehyde, anthranilic acid, and probably benzoyleneindazole. Furthermore, intramolecular pathways are favored by a factor of 11 over intermolecular pathways on the basis of GC–MS product peak abundances.

***o*-Nitrotoluene Thermolysis in Supercritical Toluene.** The rate constant for thermolysis in toluene was 2.4 times greater than for benzene. The rate increase caused by substitution of toluene for benzene is not as great as that seen for thermolysis of nitrobenzene and *p*-nitrotoluene in toluene due to the domination of intramolecular reactions in *o*-nitrotoluene. A primary KIE of 2.1 was found for *o*-nitrotoluene in toluene-d_8, supporting intermolecular reactions, and a primary KIE of 1.4 for *o*-nitrotoluene-d_3 in toluene, supporting intramolecular reactions. The product distribution differed markedly from that of benzene (Table V). Thermolysis in toluene favored the formation of toluidine, *o*-aminobenzaldehyde, and *N*-benzylidene-2-methylaniline. Anthranilic acid, aniline, benzoyleneindazole, and benzoxazinone were absent.

Table VI. Thermolysis Products from 4% 2,4-Dinitrotoluene and 4% 2,6-Dinitrotoluene in Benzene at 343 °C (80% Reacted)[a]

rel conc[b]	products
	2,4-Dinitrotoluene
2.5	2,4-diaminotoluene
100.0	biphenyl
22.5	4-nitroanthranil
20.0	*m*-nitroaniline
15.3	*x*-amino-*y*-nitrotoluene
35.8	2-amino-4-nitrobenzaldehyde
4.7	*x*-phenyl-*y*-nitrotoluene[c]
2.0	*x*-phenyl-*y*-nitroaniline[c]
4.1	1,1′:2′1″-terphenyl
2.5	1,1′:3′,1″-
4.1	1,1′:4′,1″-
	2,6-Dinitrotoluene
trace	2,6-diaminotoluene
100.0	biphenyl
73.5	6-nitroanthranil
30.0	*m*-nitroaniline
16.7	*x*-amino-*y*-nitrotoluene
6.6	2-amino-6-nitrobenzaldehyde
1.9	*x*-phenyl-*m*-nitroaniline[c]
1.2	1,1′:2′,1″-terphenyl

[a] Capillary tubes ~60% filled, identification by GC–MS. [b] Normalized to biphenyl. [c] Detected but not quantified.

The abundance of *o*-aminobenzaldehyde and *o*-toluidine, relative to the thermolysis products in benzene, shows the greater reducing power of toluene. Rearrangement to anthranil still occurred, as a primary KIE was found for *o*-nitrotoluene-d_3, but reduction of anthranil to *o*-aminobenzaldehyde was favored over formation of anthranilic acid, aniline, benzoxazinone, and benzoyleneindazole. The major thermal decomposition channels for *o*-nitrotoluene in supercritical toluene are similar to those shown in Scheme V for supercritical benzene, with the exception of benzoxazinone and anthranilic acid formations.

Thermolysis of 2,4- and 2,6-Dinitrotoluene. The rate constant for *o*-nitrotoluene is approximately doubled with the presence of another nitro group. The major thermolysis products for the dinitrotoluenes in supercritical benzene at 343 °C (Table VI) were structurally analogous to those for *o*-nitrotoluene, indicating similar thermal reactions. Intermolecular hydrogen abstraction from benzene was evidenced by an abundance of biphenyl for both dinitrotoluene isomers and a primary KIE of 1.5 for 2,6-dinitrotoluene in benzene. Intramolecular reactions were primarily evidenced by the detection of nitroanthranil. The addition of a nitro group to anthranil apparently stabilizes the heterocycle. 2-Nitroanthranil from 2,6-dinitrotoluene thermolysis was more than 3 times as abundant as 4-nitroanthranil from 2,4-dinitrotoluene thermolysis. This may be chiefly a statistical effect. Further reactions of the nitroanthranil and other intermediates were similar to *o*-nitrotoluene thermolysis.[26] The product distribution found for the dinitrotoluene thermolyses was remarkably similar to the results of a low-temperature thermolysis of TNT by Dacons et al.[58]

Thermolysis of 1,3- and 1,4-Dinitrobenzenes. Products from benzene solutions of 1,3-dinitrobenzene and 1,4-dinitrobenzene are listed in Table VII. The mechanism appears to parallel that proposed for nitrobenzene. The rate constant at 343 °C was expected to be greater than the rate constant for nitrobenzene due to the inductive effect of the second nitro group. This was not the case since the average rate constants for the dinitrobenzenes were 2–3 times less than for nitrobenzene. There is no obvious explanation for the lower rates. A solvent primary KIE of 2.9 was found for 1,3-dinitrobenzene thermolysis in benzene-d_6. Presumably, a KIE also exists for 1,4-dinitrobenzene. The mechanisms for thermolysis

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Table VII. Thermolysis Products from 4% 1,3-Dinitrobenzene and 4% 1,4-Dinitrobenzene in Benzene at 343 °C (43 and 74% reacted, respectively)[a]

rel conc[b]	products
	1,3-Dinitrobenzene
2.4	phenol
3.3	nitrobenzene
100.0	biphenyl
6.1	2-nitroaniline
3.3	3-nitrobiphenyl
78.5	4-nitrobiphenyl
4.8	1,1′:2′,1″-terphenyl
10.6	1,1′:3′,1″-
13.6	3-amino-3′-nitroazobenzene
	1,4-Dinitrobenzene
trace	nitrobenzene
100.0	biphenyl
4.2	*p*-nitroaniline
43.2	4-nitrobiphenyl
6.8	1,1′:2′,1″-terphenyl
10.6	1,1′:3′,1″-
25.5	4-amino-4′-nitroazobenzene

[a] Capillary tubes ~60% filled, identification by GC–MS. [b] Normalized to biphenyl. [c] Detected but not quantified.

of dinitrobenzene must parallel those of nitrobenzene with the rate-limiting step being hydrogen abstraction from solvent to form the dinitrobenzene–H radical.

Summary

Nitrobenzene, *p*-nitrotoluene, *o*-nitrotoluene, 2,4-dinitrotoluene, 2,6-dinitrotoluene, 1,3-dinitrobenzene, and 1,4-dinitrobenzene were thermolyzed in solution with benzene and toluene under supercritical conditions. The pseudo-first-order rate constants for the mononitroarenes in benzene are

$$k(\text{nitrobenzene}) = 1.3 \times 10^{10} \exp(-20\,051/T)\ \text{s}^{-1}$$

$$k(o\text{-nitrotoluene}) = 5.0 \times 10^{10} \exp(-19\,242/T)\ \text{s}^{-1}$$

$$k(p\text{-nitrotoluene}) = 7.9 \times 10^{9} \exp(-19\,596/T)\ \text{s}^{-1}$$

Rate constants for the dinitrotoluenes were slightly higher than for *o*-nitrotoluene but less than for nitrobenzene.

The rate-limiting step for nitrobenzene thermolysis in supercritical benzene, hydrogen abstraction from benzene, forms a charge-transfer type of a transition-state complex. This is supported by a primary KIE of 2.5, the presence of biphenyl, a ΔV^* of −46 ± 6 mL/mol, and a LFER between the logarithm of the rate constant and the solvent IP. The transient species produced from the rate-limiting step are a $C_6H_5NO_2H$ radical and a phenyl radical. A tracer study shows that some of the $ArNO_2H$ radical decomposes to $Ar^•$ and HONO. In supercritical toluene, nitrobenzene abstracts both benzylic and aromatic hydrogens. The rate constant in toluene is faster due to the resonance stabilization of benzyl radicals.

Thermolysis of *p*-nitrotoluene in supercritical benzene undergoes the same thermolysis mechanisms as nitrobenzene; the rate constants are the same, a primary KIE is present, and a similar LFER exists. The nitro group reactivity apparently is not reduced by the methyl groups' electron-donating effect. The products from *p*-nitrotoluene thermolysis are structurally related to those from nitrobenzene thermolysis. In supercritical toluene, the rate constant is faster than in supercritical benzene. The thermolysis products of the dinitrobenzenes in supercritical benzene are also analogous to both nitrobenzene and *p*-nitrotoluene, indicating similar thermal mechanisms.

o-Nitrotoluene thermolysis products in supercritical benzene show that inter- and intramolecular reactions occurred. This is supported by primary KIE's found for both deuterated solvent (1.7) and deuterated solute (1.9). Anthranil appears to be the major intermediate in the intramolecular reactions that dominate in the thermolyses. The intramolecular to intermolecular reactions ratio is approximately 11 to 1 in benzene and 1 to 2 in toluene.

The dinitrotoluenes thermolyses reactions were analogous to *o*-nitrotoluene thermolysis. Nitroanthranil is the major product in dinitrotoluene thermolysis, providing evidence of intramolecular reactions. The ratio of intramolecular to intermolecular reactions in dinitrotoluene thermolysis is approximately 5 to 1. The rate constants for *o*-nitrotoluene and the dinitrotoluenes are greater than for the nitrobenzenes and *p*-nitrotoluene due to the availability of intramolecular decomposition pathway.

The decomposition of the simple nitroarenes may serve as a model for the decomposition of more complex nitroarenes. For example, the decomposition pathways of *o*-nitrotoluene and the dinitrotoluenes are similar to the reported decomposition pathways of TNT; a primary KIE of 1.8 has been reported for TNT thermolysis in deuterated benzene[59] and of 1.7[60] when the methyl hydrogens were deuterated. 2,4-Dinitroanthranil has been reported in TNT thermolysis.[58] The TNT–H radical, analogous to the Ar–NOOH radical proposed in this study, has also been proposed on the basis of EPR studies.[51,61]

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Registry No. 1, 98-95-3; 29, 99-99-0; 41, 88-72-2; d, 7782-39-0; 2,4-dinitrotoluene, 121-14-2; 2,6-dinitrotoluene, 606-20-2; 1,3-dinitrobenzene, 99-65-0; 1,4-dinitrobenzene, 100-25-4.

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