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THERMAL STABILITY CHARACTERISTICS OF NITROAROMATIC
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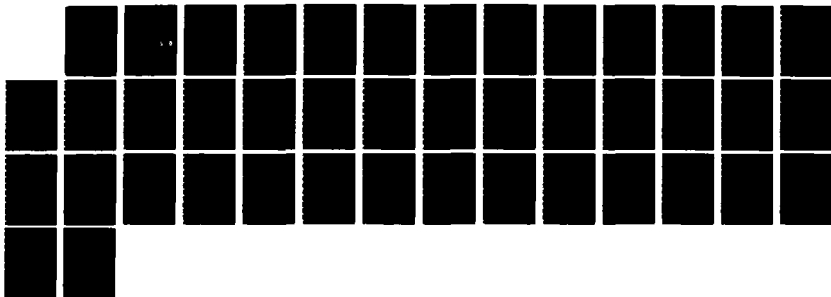
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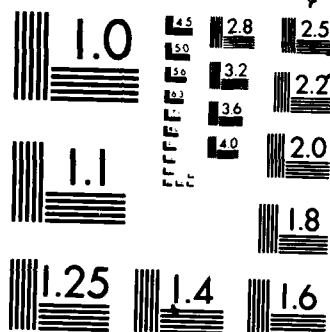
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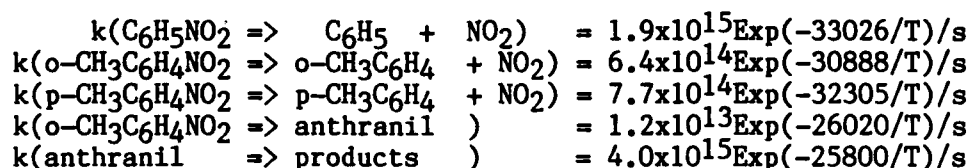
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rearrangement leading to the formation and rapid decomposition of anthranil. This represents the first report of such a process occurring purely in the gas phase and thus without the aid of acid, base or photon catalysis. It is clear that the presence of a methyl ortho to the nitro group in nitroaromatic compounds introduces a new element into the decomposition behavior of such compounds. Inasmuch as these are low activation energy processes, we expect that such reactions will be of even more importance in the lower temperature regions where ignition behavior is intimately related to the chemical kinetics.

We describe in detail the unique features of single pulse shock tube experiments and the systematic studies which permit unambiguous determination of the reaction mechanisms and the elucidation of high accuracy rate constants and expressions. The following rate expressions have been determined;



In addition, we estimate that the rate expression for the isomerization of the nitro compounds to the nitrite is approximately $10^{13} \text{Exp}(-27600/T)/\text{s}$. In conjunction with the thermochemistry we obtain a combination rate between phenyl type radicals and NO_2 of approximately 10^9 l/mol-s .

We compare our results with recent reports from laser pyrolysis studies and find disturbing differences and inconsistencies. It is suggested that there is a need for better definition of the reaction conditions under laser pyrolysis.

THERMAL STABILITY CHARACTERISTICS OF NITROAROMATIC
COMPOUNDS

FINAL REPORT

WING TSANG

SEPTEMBER 15, 1986

U. S. ARMY RESEARCH OFFICE

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CHEMICAL KINETICS DIVISION
NATIONAL BUREAU OF STANDARDS
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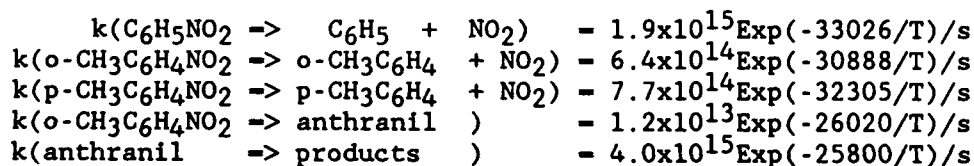
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ABSTRACT

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1. Statement of Problem

This project is concerned with the mechanisms and rates of decomposition of nitroaromatic compounds in the gas phase at temperatures near 1100 K. Experiments are carried out with a single pulse shock tube. Special attention was focussed on the on isolating the initial processes for study and in distinguishing between the various possible reaction channels.

2. Background

2.1 Past Work on Nitroaromatic Stability: There has been much interest on these and related compounds (1-5). This is due to the importance of nitroaromatic compounds as explosives, and the relationship between kinetic properties and such phenomena. Unfortunately, most of the earlier studies(1-5) have been carried out under conditions of high reactant conditions and long heating times. With the vast number of possible reaction channels in both the gas and surface it is difficult to infer mechanisms and accurate rates. Of particular concern is the initial decomposition steps. Without such information, it is not possible to discuss on a fundamental basis the detailed mechanisms and rates. It is clear that cleavage of the C-NO₂ bond is an important process. Fields and Meyerson(4) have exploited this propensity and used nitroaromatics as sources of aryl radicals. Their primary interest was preparative and reactions were carried out to high extents of completion. Thus except for the isotope labeling work it is difficult to extract quantitative kinetic information from their data. Nevertheless, the large volume of data that they have accumulated is very important and must form the basis of all subsequent work. Of particular interest in terms of the substance of this work is the drastic change in reaction product when a methyl group is ortho to the nitro. Furthermore, it is well known that ortho-nitrotoluene is much more thermally labile than the other nitrotoluenes(4). Thus in the study of Fields and Meyerson(4), aniline and anthralinic acid are detected as major products. In the work of Dacons et al(5) dinitro-anthranil was identified as an important reaction product during the decomposition of trinitrotoluene. The mechanism of how such structurally dissimilar molecules can be formed from the starting material was only cursorily addressed.

Recently, Gonzalez and coworkers (6) reported on experiments using pulse heating by an infra-red laser (Laser Enhanced Homogeneous Pyrolysis). They concluded that at 1100 K, the primary process is the breaking of the C-NO₂ bond. The rate expressions obtained are summarized in Table I. Also included are the rate constants at 1100 K. Particularly striking are the large variations in rate constants as a result of methyl substitution. Furthermore, except for a vastly increased rate methyl substitution ortho to the nitro group did not lead to any mechanistic changes. The present investigation permits a check of these results. It should be noted that the short reaction time (~10 microseconds) and the use of large excesses of chemical scavengers should lead to isolation of the primary reaction step for study. However, the technique is relatively new and there are important uncertainties regarding the exact physical conditions of the laser heated gas and whether the use of an internal standard as in the shock tube experiments can actually remove the striking inhomogeneities in both space and time that is characteristic of laser heating.

Table I: Summary of Experimental Results of Gonzalez and coworkers(6).

Process	Rate Expression/s Rate Constant/s (1100) (experimental)	RateExpression/s Rate Constant/s (1100) (corrected for fall-off)
C6H5NO2->C6H5+NO2	1.6E15xEXP(-33837/T) 70	3E15xEXP(-34340/T) 83
oNT -> oCH3C6H5+NO2	7.9E15xEXP(-32981/T) 752	2.5E16xEXP(-33736/T) 1198
pNT -> pCH3C6H5+NO2	6.3E14xEXP(-34139/T) 21	7.9E14xEXP(-34340/T) 22

2.2 Single Pulse Shock Tube: Progress in chemical kinetics in recent years have been such that the conditions necessary for the determination of the mechanisms and rates of the initial steps in the thermal decomposition of any organic molecules are known and for most substances realizable. These involve the use of dilute concentrations in short times, the use of chemical scavengers and setting the experimental configurations in such a manner so that subsequent chain processes are prevented from occurring. For this purpose the single pulse shock tube has proved to be an ideal tool(7). Systematic application of the technique has led to a complete description of the mechanism and rates of hydrocarbon pyrolysis. They have led to new values for the bond energies of simple hydrocarbons(8) and thus resolved a host of long standing controversies.

A single pulse shock tube can be regarded as a pulse heater(7) with a heating time of the order of several hundred microseconds to a millisecond, and which can operate over a wide range of temperatures, pressures and reactant concentrations. Subsequently all the reactants and products can be withdrawn for detailed analysis. We give up attempts at making real time measurement. However, the methodology for real time detection of reaction intermediates with the necessary sensitivity is currently applicable for only a very limited range of substances. This is a particular problem for studies on the decomposition of complex organics since it is rare that there are only one unambiguous reaction pathway. Furthermore, the current state of the art in the determination of trace concentrations of stable compounds are such that parts per billion are attainable with high accuracy. This permits us to work in regions where we are guaranteed clean reaction mechanisms and with a margin which permits proper tests to be made. In the following we summarize the special features of single pulse shock tube experiments.

First, since heat transfer is via a shock wave, the short residence time also guarantees the absence of any contribution from surface processes. A major source of possible errors is thus eliminated.

Second, chain processes are minimized through the lack of sufficient number of

reactive collisions when one works at appropriate conditions. This can be illustrated in the following manner. The total number of collisions that a molecule suffers in the typical conditions of a single pulse shock tube experiment (2-3 atms. pressure, 1000K and 500 microsecs. heating time) are of the order of 5 million. Since shock tube experiments are always carried out in a bath of inert gas, most of these collisions have no effect except to thermalize the system. Thus if we work with concentration of reactants in the 200 ppb range then during the course of our shock heating period, each reactant molecule can suffer only one "interesting" collision. That is, an encounter with a reactive species. It is well known that chemical reactions are rarely effected by single collisions, thus we could obviously work at somewhat higher concentrations. Furthermore, we would really like to get rid of all the reactive species during the heating period since there is always the possibility of subsequent reactions. We have therefore always carried out reactions in the presence of a chemical scavenger. This has the effect of converting the more active radicals into much less active entities, for example H-atoms into benzyl radicals from toluene. Such resonance stabilized radicals will in general recombine after the reaction period. Thus most studies are carried out with the test samples in the 100ppm range with a 100x or more excess of scavenger concentration or of the order of 1 to 10%. We can test for the effectiveness of a scavenger by varying its relative concentration with respect to the test gas. When the yields become invariant then we are assured of the proper operation of the scavenger.

Third, the thermalizing collisions help to define a proper temperature and is in contrast to certain types of laser heating experiments where the internal energy of the molecule is not coupled to that of the bath. Such experiments are extremely difficult to interpret, or alternatively one needs to make use of thermal data to determine the state of the molecule. There is no question that thermal unimolecular rate constants and expressions are being measured in single pulse shock tube experiments. These are the fundamental quantities bearing on the stability of any molecule. The absence of such information renders the proper quantitative interpretation of all other types of data highly questionable.

For quantitative work, the main uncertainty of single pulse shock tube work is the determination of the temperature of the shocked gas. Experience has shown that this is of the order of 20-30°K. This can easily lead to uncertainties of a factor of 2 or three in absolute rate constants. We have circumvented this through the use of an internal standard. This involves shocking in the same gas mixture two compounds. The first is the "unknown" and the second a substance whose rate constant for unimolecular reaction has been established from other measurements. The fact that our scavenger "protects" one reactant from secondary processes means that our "standard" will similarly be protected. Thus from the extent of decomposition of the standard an average reaction temperature can be derived. This has proved to be highly successful(7) and at the present time rate constant determined by this methodology are among the most accurate of high temperature values.

The fact that we can only detect stable products sets the constraint that if an unstable intermediate is formed then a means must be provided for its conversion to a stable species during the heating period. Two alternatives are possible. In one case the intermediate may be so unstable so that they decompose to a stable compound during the heating period. This is the situation for the alkyl radicals.

They decompose quantitatively to the alkenes and we have used this property extensively in order to determine the rate expression for the decomposition of scores of aliphatic compounds. Alternatively, the intermediate may be so thermally stable such that under our heating conditions no decomposition channels are available. In those cases we have provided a source of abstractable hydrogen atoms so as to convert the intermediate into the hydrogenated species. Such a scavenger is cyclopentane and we have used it to trap CF_3 and Br (9,10). In the next section we will demonstrate that it can play a similar role with regard to phenyl radicals.

3. Approach

We begin our investigation with a study on iodobenzene and o-iodotoluene decomposition. These essentially preliminary studies are concerned with the reactivity and stability of the phenyl and orthomethylphenyl radical and establishes the conditions under which we can quantitatively trap all of the phenyl type radicals that are released into the system. We also deal with the establishment of a calibrant for our subsequent quantitative measurements. Furthermore, we are able to establish a tie-point with previous work through direct comparison of measured rate constants and the thermochemistry. This permits an assessment of the validity of the subsequent work. We then consider C- NO_2 bond breaking and NO_2 isomerization reactions in nitrobenzene, o-nitrotoluene and p-nitrotoluene decomposition. In the course of this work, we established that the mechanism of o-nitrotoluene decomposition differed considerably from that of the other two compounds. Therefore, it was necessary to consider the mechanism of o-nitrotoluene decomposition in greater detail. This leads to a study of the formation (from o-nitrotoluene decomposition) and destruction of anthranil.

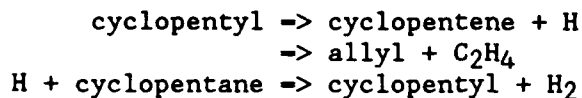
4. Decomposition of Iodobenzene and Iodotoluene

4.1 Experimental: Our studies are carried out in a heated single pulse shock tube that we have recently assembled. Except for the fact that it is made from square 1.25" aluminum tubing it is similar to that used in our earlier experiments(7). The low pressure section was heated by heating tape wound about an outer 6" aluminum tube. Temperatures were maintained at $100 \pm .5^\circ\text{C}$. The driver section and the entire gas handling system were also heated and maintained at an elevated temperature over the course of all the experiments. Heating the entire system enabled us to introduce and extract from the shock tube compounds of low volatility.

Analysis of reactant and product gases is by gas chromatography with flame ionization detection. The columns used are six feet bentone at 100°C and 12 feet silicone oil at 88°C . They are connected in such a way that all compounds up to the iodoaromatics are eluted in a reasonable time. The iodo-compounds and the cyclohexenes are from SCM(11). The cyclopentane is from Wiley Organics and the Argon is of Ultrapure Grade and is from Matheson. Gas chromatography failed to reveal the presence of any impurity in the test gas. Thus except for vigorous degassing of the organic samples no attempt was made at further purification. The internal standard used for these studies is the reverse Diels-Alder decomposition of 1,2 dimethylcyclohexene (1,2DMC) to form ethylene and 2,3 dimethylbutadiene. This reaction was selected because with the chromatographic

columns used in the present experiments, the 2,3 dimethylbutadiene eluted in a convenient time. Since rate expressions for this reaction does not exist, the first studies involved comparative rate experiments on the decomposition of 1,2 dimethylcyclohexene using as internal standards the decomposition of cyclohexene (CH) and 1-methylcyclohexene(1-MCH)(7).

Crucial to the success of these experiments is the effectiveness of cyclopentane as a radical scavenger. This involves not only its reactions with reactive species but also the stability of the cyclopentyl radical. The latter decomposes via the reactions,



The allyl radical is fairly stable within the time scale of these experiments (500 microsecs). Furthermore, as long as the cyclopentane remains in large excess, the phenyl iodide is protected from radical induced decomposition, unless the rates of radical attack on cyclopentane is much slower than on phenyl iodide. The effectiveness of cyclopentane as an inhibitor against such processes has been demonstrated in an earlier study(9,10). There we showed that in the decomposition of $\text{BrC}_2\text{F}_4\text{Br}$ in cyclopentane at temperatures up to 1100K exactly two ethylene molecules are formed for every perfluorethylene molecule detected. In the present case we are using the cyclopentane as a source of hydrogen atoms for phenyl and o-methylphenyl radicals. The conditions under which quantitative conversions to benzene or toluene occur can then be used in subsequent studies to account for the number of phenyl type radicals in a reactive system.

Of key importance to the quantitative validity of these experiments is the necessity for the complete conversion of all the phenyl radicals to benzene. Unfortunately, data on the reactivity of phenyl radicals are scarce. In order to attest to complete conversion, experiments have been carried out with a whole range of cyclopentane concentrations. The ratio of cyclopentane to the aromatic iodide concentrations varied between 100 and 300. The cyclopentane concentration varied from .1 to 5%. The reaction pressure ranged from 2-6 atms. The large excess of cyclopentane serves as a radical trap and makes impossible the radical induced decomposition of the iodoaromatic compounds. It is expected that as the cyclopentane concentration is reduced there will come a point below which phenyl radical conversion to benzene will be incomplete. This will be demonstrated by failure in material balance and systematic deviations in the comparative rate plots. It will permit a limit to be set on the minimum level of cyclopentane for our purposes.

In earlier studies with cyclopentane as the scavenger, the yields of ethylene also served as a marker for the number of radicals released into the system. This did not prove to be feasible in the present instance, because the rate constant for iodine attack on cyclopentane is sufficiently slow so that there is considerable uncertainty as to whether all the iodine radicals can be trapped in this manner. Furthermore, the aromatic iodides used in these studies are considerably more stable than the allyl bromide and dibromoperfluoroethane used in our earlier studies. Thus the 1100 K limit beyond which the decomposition products from cyclopentane pyrolysis will begin to have an interfering effect on

the light hydrocarbon yields must be exceeded. Our experiments are carried out in the 1050-1200K range. At the higher temperature end of this range, our previous(12) studies have demonstrated that the direct products from cyclopentane decomposition (present in 100-300 fold excess over the aromatic iodide) is close to or may even exceed the light hydrocarbon yields originating from the induced decomposition of the cyclopentane (due to aromatic iodide decomposition). However, cyclopentane decomposition under the present conditions does not form benzene. Benzene formed in these experiments must have originated from phenyl radicals. Demonstration of proper material balance also implies the possibility of using the benzene yield as a marker of reaction extent. Accordingly we focus attention in these experiments on the quantity of benzene or toluene formed, the amount of phenyliodide or ortho-methylphenyliodide lost and the yields of 2,3dimethylbutadiene from the decomposition of the standard.

4.3 Results: The initial studies involve the determination of the rate parameters for the decomposition of the internal standard, 1,2 dimethylcyclohexene(1,2 DMC). The results of comparative rate experiments with cyclohexene (CH) and 1-

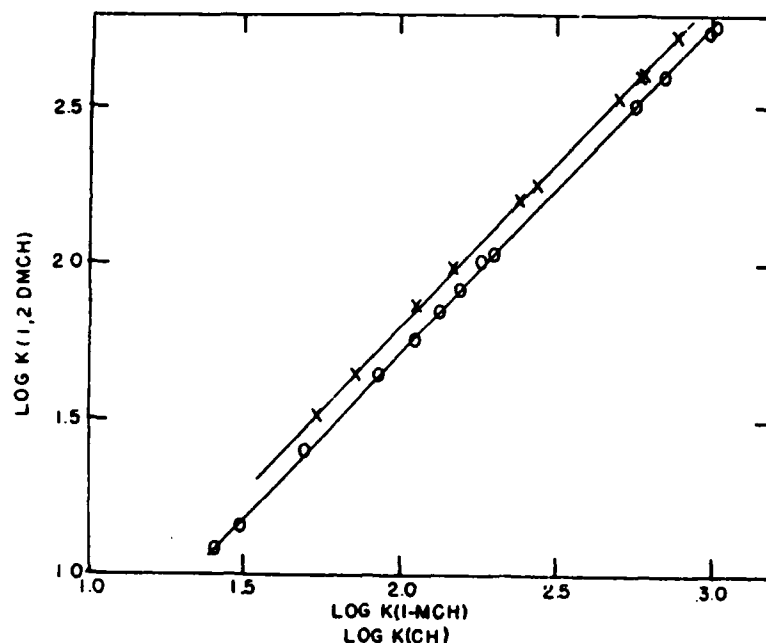


Figure 1: Comparative Rate Single Pulse Shock Tube Results on the Decomposition of 207 ppm 1-Methylcyclohexene(1-MCH) and 207 ppm 1,2-Dimethylcyclohexene(1,2DMCH) in 5% Toluene and Argon (X) and 290 ppm Cyclohexene(CH) and 204 ppm 1,2-Dimethylcyclohexene (1,2DMCH) in 5% Cyclopentane and Argon(O). Reaction pressure is approximately 3 atmospheres. Temperature, 1060-1200K. Heating time, 500 microsec.

methylcyclohexene (1-MCH) decomposition as calibrants and with the butadienes as the markers for the extent of reaction are plotted on Figure I. The least squares relations are as follows;

$$\begin{aligned} \text{Log } k(1,2\text{DMC}) &= (1.052 \pm .003) \text{ Log } k(\text{CH}) - (.392 \pm .007) \\ \text{and } \text{Log } k(1,2\text{DMC}) &= (1.049 \pm .005) \text{ Log } k(1\text{-MCH}) - (.305 \pm .01) \end{aligned}$$

Using $k(\text{CH}) = 1.4 \times 10^{15} \text{Exp}(-33535/T)$ and $k(1\text{-MCH}) = 1.1 \times 10^{15} \text{Exp}(-33535/T)/\text{s}$, (3) we arrive at, $k(1,2 \text{ DMC}) = 3.5 \times 10^{15} \text{Exp}(-35278/T)/\text{s}$ with the cyclohexene standard and $k(1,2\text{DMC}) = 3.0 \times 10^{15} \text{Exp}(-35178/T)/\text{s}$ with the 1-methylcyclohexene standard. The expression that will be used in the subsequent analysis,

$$k(1,2\text{DMC} \rightarrow \text{C}_2\text{H}_4 + 2,3\text{DMB}) = 3.2 \times 10^{15} \text{Exp}(-35228/T)/\text{s}$$

is the average of the results of the two sets of experiments. It is interesting that there is a distinct difference in the rate expression for 1,2 dimethylcyclohexene decomposition as compared to the other two cyclohexenes. The results from the two independent set of experiments appear to confirm the unexpected result. Due to the molecular nature of these experiments the extra uncertainty introduced by the use of a "secondary" standard should be small. It is estimated that this will not exceed 1 kJ in the activation energy and a factor of 1.15 in the A-factor.

The products from the decomposition of the aromatic iodides in the presence of large excesses of cyclopentane are ethylene, propylene, allene, 1-pentene and benzene (or toluene in the case of orthoiodotoluene decomposition). Ethylene is the most prominent reaction product. The aromatic compounds are also present in large quantities. As expected a significant amount of the ethylene and propylene comes from the thermal unimolecular decomposition of cyclopentane itself (through 1-pentene)(12). The results summarized in Table II demonstrate the nature of the mass balances that can be obtained. For phenyl iodide, it can be seen that only at the lowest cyclopentane concentration is there a significant mass defect. The relationship between fractional conversion to benzene (F), rate constant for abstraction(k) and scavenger concentration (C) can be expressed to a very good approximation as

$$F = 1 - (1 - \text{Exp}(kCt))/kCt$$

where t is the residence time and is of the order of 500 microsec. The data in Table II show that at a cyclopentane level of 0.1% we recover approximately 60% of the missing phenyliodide as benzene. This means that $kC = 6 \times 10^3/\text{s}$. Most of the experiments have been carried out with cyclopentane concentrations of a factor of 50 higher. Here kC is equal to $3 \times 10^5/\text{s}$ and substitution into the above relation suggest conversions of greater than 99%. Indeed, even with 1% cyclopentane conversion exceeds 95%, as shown by our data in Table II. An important problem in single pulse shock tube experiments is the invariance of the heating time. Thus near the low temperature limit (~1050 K) and correspondingly low conversions it is difficult to draw conclusions about mass balance by simply comparing product appearance and reactant disappearance. It is however possible to make some inferences on the basis of the comparative rate plots, where we compare the rate constant for unimolecular decomposition of our test molecule against the internal standard.

Table II: Mass Balances at Higher Extents of Decomposition for Iodobenzene (IBz) and Ortho-Iodotoluene (ITol) at 1175K, 3 atm pressure and 500 microsec. heating time.

	$RH/(RI)1$	$(RI)f/(RI)1$	$(RH+(RI)f)/(RI)1$
a) Iodobenzene			
5.1% cyclopentane	.263	.730	.993
181 ppm IBz			
1% cyclopentane	.262	.738	1.00
35 ppm IBz			
.2% cyclopentane	.222	.761	.983
6.9 ppm IBz			
.1% cyclopentane	.183	.701	.884
3.4 ppm IBz			
b) Orthoiodotoluene			
5% cyclopentane	.267	.720	.987
216 ppm ITol			

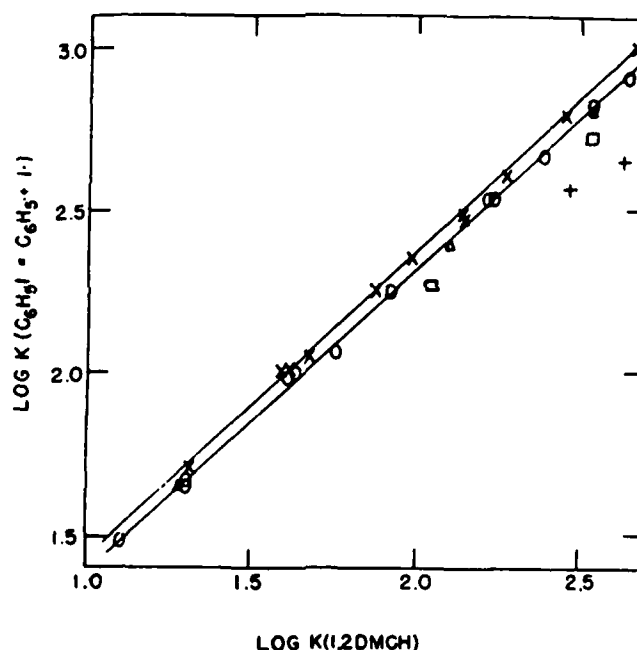


Figure II: Comparative Rate Single Pulse Shock Tube Results on the Decomposition of Iodobenzene ($C_6H_5I \rightarrow C_6H_5 + I$) with 1,2Di- methylcyclohexene Decomposition as the Internal Standard and Cyclopentane as the Scavenger in Argon. 2-6 atms. pressure. Temperature, 1000-1200K. Heating time, 500 microsec.

Iodobenzene	1,2 Dimethylcyclohexene(1,2DMC)	Cyclopentane
181 ppm	222 ppm	51000 ppm (O)
110 ppm	358 ppm	49000 ppm (X)
35 ppm	45 ppm	10000 ppm (Δ)
7 ppm	9.0 ppm	2000 ppm (□)
3.4 pp	4.3 ppm	1000 ppm (+)

Figure II represents the results of studies on phenyl iodide. It consists of experiments with two different ratios of 1,2dimethylcyclohexene and iodobenzene in very large excesses of cyclopentane. The experiments that contain the highest cyclopentane to iodobenzene ratio show a systematic deviation of 10% in the relative rate plots. This is about twice the standard deviation and is thus statistically significant. We are not certain of the cause of this discrepancy. It should have a minimal effect on our final results, since as can be seen in Figure II the comparative rate plots parallel each other and thus the changes in the rate expressions are insignificant within the context of these experiments. At a fixed iodobenzene to 1,2 dimethylcyclohexene to cyclopentane ratio no effect on the comparative rate plot could be observed when cyclopentane concentration is lowered to 1%. However, below this level deviations become increasingly large. This is in accord with our earlier discussion.

We conclude that the rate constant we calculate on the basis of the benzene and toluene yield faithfully reflects the rate of bond cleavage in phenyl iodide and orthiodotoluene respectively. The least squares relation from the comparative rate experiments with 36-180 ppm iodobenzene, 46-230 ppm 1,2dimethylcyclohexene and 1-5% cyclopentane in argon leads to

$$\text{Logk}(\text{C}_6\text{H}_5\text{I} \rightarrow \text{C}_6\text{H}_5 + \text{I}) = (.930 \pm .006)\text{Logk}(1,2\text{DMC}) + (.456 \pm .012).$$

For studies with 110 ppm iodobenzene and 358 ppm 1,2dimethyl-cyclohexene in 5% cyclopentane and argon we obtained

$$\text{Logk}(\text{C}_6\text{H}_5\text{I} \rightarrow \text{C}_6\text{H}_5 + \text{I}) = (.934 \pm .007)\text{Logk}(1,2\text{DMC}) + (.504 \pm .015).$$

Thus except for the 10% deviation mentioned earlier, the relations are identical. Substitution into these relations the rate expression for 1,2 dimethylcyclohexene decomposition derived earlier leads to the following average rate expression;

$$k(\text{C}_6\text{H}_5\text{I} \rightarrow \text{C}_6\text{H}_5 + \text{I}) = 8.6 \times 10^{14} \text{Exp}(-32821/T)/\text{s. at } 1100\text{K}$$

It should be noted that in our comparative rate experiments the pressure was varied by a factor of 3. Failure to observe any significant pressure dependence is indicative of our being at or very close to the high pressure limit. From earlier studies(7) across such a pressure range we have established that a pressure dependence of the order of $p^{0.05}$ could be observed. There is no question that 1,2 dimethylcyclohexene decomposition is at the high pressure limit(7)

Comparative rate plots of the decomposition of orthiodotoluene using phenyliodide decomposition as the internal standard can be found in Figure III. In these studies we use the benzene and toluene yields as markers for reaction extent. The rate relationship is,

$$\text{logk}(\text{o-CH}_3\text{C}_6\text{H}_4\text{I} \rightarrow \text{o-CH}_3\text{C}_6\text{H}_4 + \text{I}) = (1.016 \pm .022)\text{Logk}(\text{C}_6\text{H}_5\text{I} \rightarrow \text{C}_6\text{H}_5 + \text{I}) - (.031 \pm .054)$$

This leads to,

$$k(\text{o-CH}_3\text{C}_6\text{H}_4\text{I} \rightarrow \text{o-CH}_3\text{C}_6\text{H}_4 + \text{I}) = 1.4 \times 10^{15} \text{Exp}(-33346/T)/\text{s at } 1100\text{K}$$

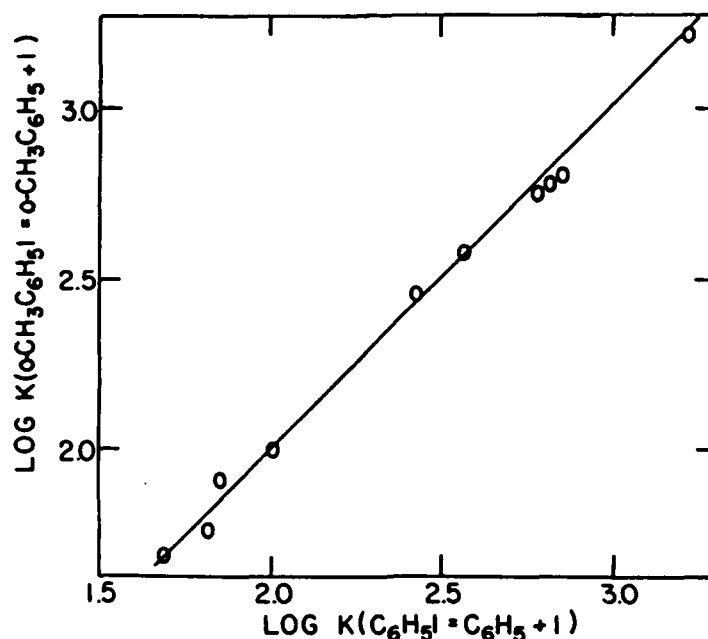


Figure III: Comparative Rate Single Pulse Shock Tube Results on the Decomposition of Iodobenzene (229 ppm) and o-Iodotoluene (216 ppm) with 5% Cyclopentane as the Scavenger in Argon. 3 atms. Reaction Pressure. Temperature, 1000-1220K.

4.4 Discussion: The rate expression for phenyl iodide decomposition that we have determined is in satisfactory agreement with that determined by Kominar, Krech and Price(13). Extrapolating our results to the lower temperature range where they carried out their experiments, we find $k(\text{C}_6\text{H}_5\text{I} \rightarrow \text{C}_6\text{H}_5 + \text{I}) = .19/\text{s}$ at 910k. This can be compared with the value of .31/s as determined from the flow experiment. In absolute magnitude there is a discrepancy of a factor of 1.6. We are uncertain of the cause of this difference. It is our experience that the uncertainty in the rate constant from single pulse shock tube experiments is of the order of a factor of 1.3. It is possible that the flow experiments may have errors arising from uncertainties in the flow rates and reaction temperatures. There has been no previous studies on the decomposition of ortho-iodotoluene. Our studies establish that methyl substitution has virtually no effect in either a mechanistic or quantitative sense. Note that the rate constant at the reaction temperature for the phenyl iodide and o-iodotoluene decompositions are for practical purposes identical. It is suspected that the differences in rate expressions is to a large extent due to experimental errors. The smallness of the observed effect is somewhat surprising. In the decomposition of substituted alkanes(9) we have found that the effect of beta-methylation can lead to changes of rate constants of a factor of 2 in the rate constant for C-C bond cleavage.

It is usually assumed that for such simple bond breaking reactions the activation energy is related to the bond dissociation energy at the reaction temperature

through the relation $\Delta H(\text{reaction}) = \Delta E(\text{exp.}) + RT$. Implicit in this relation is the assumption that the activation energy for the bond forming process is zero in concentration units(7). For phenyl iodide our results give $\Delta H(\text{reaction}) = 281.9$ kJ at 1100K. Since $\Delta H_f(\text{C}_6\text{H}_5\text{I}) = 117.6$ kJ/mol (14) and $\Delta H_f(\text{I}) = 77.2$ kJ/mol (15) at 1100K, we find $\Delta H_f(\text{C}_6\text{H}_5) = 322.3$ J/mol at 1100K. Using the recently tabulated values (16) for the heat capacity of phenyl radical, where it is assumed that the only difference in the heat capacity of phenyl and benzene arises from the deletion of the vibrational frequencies associated with the hydrogen atom that has been removed from the latter, we find $\Delta H_f(\text{C}_6\text{H}_5) = 340.5$ kJ/mol at 300K. This is 12 kJ/mol higher than the value recently recommended by McMillen and Golden (17) of $\Delta H_f(\text{C}_6\text{H}_5) = 328.4 + 8$ kJ/mol. However, in view of an estimated uncertainty of 11 kJ/mol from our measurements; arising from a 6 kJ/mol uncertainty in the heat of formation of the phenyl iodide (14) and a 5 kJ/mol uncertainty from our measurements, the significance of this difference is unclear. It does raise the possibility that the C-H bond dissociation energy in benzene will have to be raised to 475.3 kJ/mol. On the other hand, the recommendation of McMillen and Golden is not only based on the iodination studies (18) but also on the work of Chamberlain and Whittle (19) on the kinetics of the reactions, $\text{CF}_3 + \text{C}_6\text{H}_6 \rightleftharpoons \text{C}_6\text{H}_5 + \text{CF}_3\text{H}$ from which they obtained a heat of formation of the phenyl radical of 325 ± 8 kJ/mol. Since their procedure involved essentially a third law analysis and we have verified their calculations, one would usually prefer such a value. However the data(20) on the phenyl radical abstraction process (based on diphenylmercury photolysis) is not completely satisfactory. For example, their reported rate constant for phenyl radical attack on methane is a factor of four higher than that published in another study (21) that is based on acetophenone photolysis. Thus a consequence of our higher value for the heat of formation of the phenyl radical is the possibility that the very small data base on phenyl radical abstraction reactions may be subject to serious errors (close to an order of magnitude). The above is illustrative of the serious consequences that can arise in rate constants and equilibrium constants from what would appear to be small uncertainties in the heat of formation. Finally, for completeness we also mention the heat of formation of phenyl (300 K) as determined by Rosenstock et al(22) of 330 ± 13 kJ/mol, from photoelectron-photoion coincidence mass spectrometry, and Kiefer et al(23), from high temperature shock tube studies, of 335 ± 8 kJ/mol. There is clearly room for more accurate determinations.

In spite of these uncertainties, our results can lead to an estimate of the reverse combination process between phenyl radicals and iodide atoms. The spread in the heat of formation of 12 kJ leads to an uncertainty in the results of a factor of 3. Assuming the entropies of the phenyl radical as tabulated by Burcat et al(16), then if we use the heat of formation as recommended by McMillen and Golden, we find a combination rate of 4.8×10^9 l/mol-s, while for our higher heat of formation we arrive at a rate constant of 1.5×10^{10} l/mol-s. The rate constant is thus very close to that for $\text{CF}_3 + \text{Br}$ (9), but about an order of magnitude smaller than what we have found for alkyl and resonance stabilized radicals with bromine and iodine atoms(10).

Our failure to obtain a satisfactory mass balance at the lowest cyclopentane concentrations permits us to set an upper limit for the rate constant for phenyl radical attack on cyclopentane. Thus from our earlier analysis $kC = 6 \times 10^3/\text{s}$, where k is the rate constant for abstraction and C is the concentration of

cyclopentane. The value of the latter is 1.2×10^{16} molecules/cc, This leads to

$$k(\text{phenyl} + \text{cyclopentane}) \leftarrow 3 \times 10^8 \text{ l/mol-s}$$

at 1100K. This is close to a factor of 30 higher than the extrapolated rate constant for methyl attack on cyclopentane. This difference may be somewhat diminished if we take into account the possibility of non-linear Arrhenius behavior and the possibility of reaction occurring after the heating period. Nevertheless, the results are indicative of a very reactive phenyl radical. This is in line with the highly exothermic nature of the abstraction reaction.

5. C-NO₂ Bond Cleavage in the Decomposition of Nitroaromatic Compounds

5.1 Experimental: The experimental procedure is exactly the same as used in our iodobenzene and iodotoluene studies.

5.2 Analysis and Results: Initial experiments are carried out with nitrobenzene. These are designed to obtain information on mechanisms. Table III summarizes the results carried out with a variety of concentrations of nitrobenzene and cyclopentane. It can be seen that the important products are ethylene, propylene, benzene and phenol. Also included are the concentrations of nitrobenzene that remained after the reaction. The study on iodobenzene and o-iodotoluene decomposition has established that the integrity of the aromatic ring structure is maintained under the conditions of these experiments. Comparisons of the phenol and benzene yields with the nitrobenzene remaining after the heating period lead to a fairly good mass balance. Nevertheless, at the higher extent of reaction, some of the nitrobenzene is not accounted for.

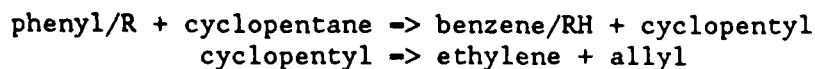
Of particular mechanistic interest is the presence of phenol. It can be formed by three possible mechanisms. First, the phenyl radical may react with the NO₂ that is formed as a result of the C-NO₂ bond breaking reaction. This leads to a phenoxy radical which can then react with the scavenger to form phenol. Second, the nitrobenzene can isomerize into the nitrite. Since the O-NO bond is known to be very weak (17), under shock tube conditions it will immediately break and lead to the formation of a phenoxy radical and ultimately phenol in the same manner as described above. Finally, if OH is formed in this system (with H-atoms and NO₂ present, this is a likely possibility) displacement of NO₂ by OH may occur. Our experiments with varying relative and absolute concentrations of nitrobenzene and cyclopentane permit an unambiguous choice among the different possibilities. Thus, when the absolute concentration of nitrobenzene is increased while that of cyclopentane is unchanged the ratio of benzene to phenol is relatively invariant. This clearly cannot be the case if phenol is formed via displacement by OH or through reaction of phenyl with NO₂. In both cases the increased levels of nitrobenzene should lead to increased levels of OH and NO₂ and thus larger amounts of phenol. The significant decrease in the yields of phenol when the absolute concentrations of reactants are decreased but with the relative amount fixed supports the hypothesis that phenol must be formed from a phenoxy predecessor. It also demonstrates that we are still in the kinetic region with respect to phenol formation. Cyclopentane is not present in sufficient amount so as to convert all the phenoxy radicals to phenol. This is not unreasonable since

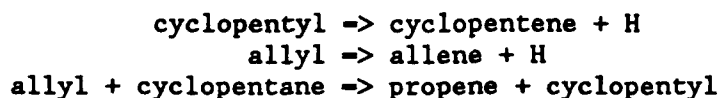
Table III. Relative Amounts of Major Products from the Decomposition of Nitrobenzene(NB) in Cyclopentane(CP), 450 microsecs heating time.

Mixtures	$\frac{100C_2H_4}{(NB)1}$	$\frac{100C_3H_6}{(NB)1}$	$\frac{100C_6H_6}{(NB)1}$	$\frac{100C_6H_5OH}{(NB)1}$	$\frac{100(NB)f}{(NB)1}$	T(K)	P(atm)
804 ppm NB in 8.3% CP and Argon	16.2	2.49	5.22	.87	94.5	1089	4.1
	38.4	5.47	11.94	2.23	85.9	1122	4.1
	180.9	43.5	43.5	6.84	40.0	1190	4.3
	139.6	28.6	38.2	6.1	50.0	1180	4.3
	52.3	7.5	16.0	2.9	80.5	1134	3.9
132 ppm NB in 1.4% CP and Argon	140	12.2	42.4	2.3	39.0	1188	2.6
	72.7	5.3	24.2	1.5	64.5	1153	2.7
	4.9		2.3		95.6	1060	2.4
	81.8	6.1	26.5	1.9	58.5	1159	2.7
	9.8	.8	4.5		94.5	1084	2.4
	52.3	3.8	19.7	1.1	66.5	1124	2.7
3572 ppm NB in 9.56% CP and Argon	48.9	5.6	17.4	3.4	74.0	1139	4.3
	95.9	14.0	33.2	6.2	49.0	1172	4.4

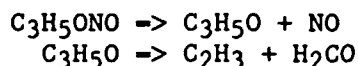
phenoxy radical is expected to be less reactive than phenyl in abstraction processes. Thus some of the missing aromatic type compounds can be accounted for as unconverted phenoxy radical. On this basis we can postulate that the important initial processes in the thermal decomposition of nitrobenzene are C-NO₂ bond cleavage to form phenyl and isomerization to the nitrite followed by O-NO bond cleavage to form phenoxy.

We next consider the presence of propene and ethylene. Although these are the products from the thermal decomposition of cyclopentane(12), the temperatures at which these studies are carried out are sufficiently low so that only a minor amount of these compounds could be formed from this source. This is validated by the constant ethylene to benzene ratio with variations in relative amounts of cyclopentane and nitrobenzene. Instead, they must be formed from the radical induced decomposition of cyclopentane. The specific reactions are,





where R is any radical and phenyl also includes methylphenyl radicals. Allyl radicals are however reasonably stable under the present experimental configuration and although they can undergo reactions of the type listed above, the rates are sufficiently small so that long chains are not possible. Our failure to find significant quantities of allene is partial evidence of this. In any case cyclopentane decomposition under our conditions can never lead to benzene formation. Thus as long as cyclopentane concentrations are present in large excess and the relative rates of radical attack on the nitroaromatics and cyclopentane are not widely different, then the former is in essence "protected" from radical induced decomposition. Our hypothesis regarding propene formation as a result of H-atom abstraction from cyclopentane by allyl is supported by the decrease in propylene produced when the absolute quantities of cyclopentane and nitrobenzene is reduced. Here as in the phenoxy case we see a manifestation of the decreased reactivity of the resonance stabilized radicals. Ethylene is present in three fold excess compared to benzene. Even after subtracting the ethylene that can be formed from the abstraction process involving allyl and phenoxy radicals there is still a 2.5 fold excess. We have demonstrated in an earlier publication(9) that for every reactive radical released into the system one ethylene must be formed. In the present instance every phenyl radical can only lead to one ethylene. The excess ethylene must be assigned to reactions involving the NO₂ molecule. A possible mechanism involves the abstraction of a hydrogen from cyclopentane by NO₂ and then the decomposition of the newly formed nitrous acid. Note that the HO-NO bond energy in nitrous acid is of the order of 200 kJ/mol and the molecule can be expected to be unstable under our reaction conditions. Alternatively, allyl radicals may react with NO₂ to form the nitrite which will rapidly decompose through the following sequence of reactions;



The vinyl radical can abstract a hydrogen atom from cyclopentane to form ethylene while the decomposing cyclopentyl radical will also release an ethylene. It may also decompose to form acetylene and from the attack of H-atoms on cyclopentane release another ethylene molecule. In our experimental configuration we do not separate the two C₂ unsaturates. All of the above provides a convincing explanation of the excess C₂ hydrocarbons that we observe.

Table IV contains the product distribution from the decomposition of para-nitrotoluene. It can be seen that except for the substitution of toluene for benzene the relative amounts of products and the percentage of toluene recovered closely paralleled the situation for nitrobenzene decomposition. Experimental difficulties prevented us from measuring para-cresol, but the results certainly justify the assumption that it will parallel the nitrobenzene decomposition mechanism. Table V gives the product yields from ortho-nitrotoluene decomposition. Much to our surprise less than one-third of the ortho-nitrotoluene that has disappeared is recovered as toluene. As a first check of this unexpected result we carried out a number of experiments with different scavengers. The results are summarized in Table VI and include data using C₆F₅CH₃, the scavenger

Table IV: Relative Amounts of Major Products from the Decomposition of p-Nitrotoluene(pNT) in Cyclopentane(CP). 450 Microsecs. Heating Time.

Mixtures	$\frac{100C_2H_4}{(pNT)_1}$	$\frac{100C_3H_6}{(pNT)_1}$	$\frac{100CH_3C_6H_5}{(pNT)_1}$	$\frac{100CH_3C_6H_4OH}{(pNT)_1}$	$\frac{100(pNT)_f}{(pNT)_1}$	T(K)	P(atm)
148 ppm pNT in 434ppm DMC and 5.2% CP in Argon			34.9		46	1185	3.8
			34.8		43.5	1185	4.0
			16		77	1142	4.0
			9		89	1116	3.4
			13.3		82.7	1133	4.1
	22.2	4.6	6.1			1101	4.2
	22.5	4.8	6.2			1101	4.4
	61.2	13.5	15.0			1138	3.8
165ppm pNT in 5.2% CP and Argon			5.8		91	1095	3.4
			32		48	1180	3.5

employed by Gonzalez and coworkers(6). It can be seen that in all cases the mass deficit is even larger than we found with cyclopentane as the scavenger. In addition, we call attention to the very satisfactory mass balance that was achieved when ortho-iodotoluene was decomposed. We are led to the inescapable conclusion that in ortho-nitrotoluene decomposition there is a competitive reaction channel which is of greater importance than C-NO₂ bond cleavage.

Also included in Table V is an experiment where we monitored the yield of ortho-cresol. It is clear that this is not the alternative reaction channel. Indeed, the relative amount of ortho-cresol in comparison to the toluene is more or less the same as that for phenol and benzene in nitrobenzene decomposition. This then leaves more than half of the decomposition products unaccounted for. We have searched for additional peaks by carrying out the chromatographic analysis over much longer periods of time than needed to elute the compounds discussed in the previous paragraphs. No significant new peaks were discovered. It is concluded that the products are not passing through the columns that we are using.

Finally, we consider the yields of C₂ and propylene as given in Table V. Note that in comparison to toluene the smaller hydrocarbons are present in considerably larger quantities than the para-nitrotoluene or nitrobenzene. These results indicate that our unknown reaction process releases reactive radicals into the system. On the other hand, the incremental amount is less than the 2.5 to 1 that characterized the C₂ hydrocarbons and the aromatics in the nitrobenzene

Table V: Relative Amounts of Major Products from the Decomposition of o-Nitrotoluene(oNT) in Cyclopentane(CP). 450 microsecs. heating time

Mixtures	$\frac{100C_2H_4}{(oNT)_i}$	$\frac{100C_3H_6}{(oNT)_i}$	$\frac{100CH_3C_6H_5}{(oNT)_i}$	$\frac{100CH_3C_6H_5OH}{(oNT)_i}$	$\frac{100(oNT)_f}{(oNT)_i}$	T(K)	P(atm)
166 ppm oNT in			20		37.6	1121	4.1
647ppm DMC and			8.4		71.0	1073	3.9
5.2% CP in			11.3		61.0	1087	4.0
Argon							
	69.1	9.9	11.9			1091	4.0
	78.6	11.9	13.6			1099	4.1
	48.5	6.6	8.2			1072	4.0
			9.4		67.0	1079	4.1
			19.3		40.5	1118	4.4
				6	25	1150	4.5
158ppm oNT in			9.7		65	1082	3.5
4.9% CP and			4.8		84	1057	3.5
Argon			4.1		86.5	1051	3.6

Table VI. Recovery and Reactant Loss During o-Nitrotoluene Decomposition in the Presence of Various Inhibitors

Mixtures	$\frac{100(C_6H_5CH_3)_f}{(o-NT)_i}$	$\frac{100(o-NT)_f}{(o-NT)_i}$
1. 193.5 ppm o-Nitrotoluene and 298.1 1,2 DMC in 2.5% methylfluorobenzene	1.1 11.9	94 33
2. 167 ppm o-Nitrotoluene in 5.4% Propyne	5.8 3.8	57 75

and para-nitrobenzene cases. We conclude that the major decomposition channel in ortho-nitrotoluene decomposition does not involve either C-NO₂ decomposition or an isomerization process. Radicals are released into the system. The aromatic ring is probably not being fragmented into C₂ or C₃ species. Any large organic species must either rapidly polymerized or may still contain nitrogen or oxygen structures. Such compounds will be difficult to detect under the present conditions. We are currently carrying out experiments to clarify such possibilities.

The present results do permit an accurate determination of the rate expressions for C-NO₂ bond cleavage. The relevant relation is;

$$k(\text{C}_6\text{H}_5\text{NO}_2 \rightarrow \text{C}_6\text{H}_5 + \text{NO}_2) = \ln(1 - \text{benzene} \cdot X / \text{C}_6\text{H}_5\text{NO}_2) / tX$$

where t is the residence time and X is equal to

$$1 + (\text{other primary reactive products} / \text{benzene})$$

where the (other reactive primary products) is obtained from mass balance considerations. It is therefore a measure of the contributions from the alternative reaction channels. Note that at low conversions, their effect on the rate constant disappears. Thus to a very good approximation there is no need to determine exactly the branching ratio at all extents of reaction. In the present treatment of the data we have simply used the value of the branching ratio at the highest conversions. Note that the expression given above is for the decomposition of nitrobenzene. For the other two systems toluene must of course be substituted for benzene.

The results of comparative rate experiments with 1,2dimethylcyclohexene(1,2DMC) decomposition as the internal standard can be found in Figures IV-VI. In the case of nitrobenzene decomposition, Fig IV, we have carried out experiments with a wide variety of mixture compositions. The fact that all our results fall on the same line supports our mechanism and is a graphic demonstration that under our conditions the benzene yield is a direct measure of the initial C-NO₂ bond cleavage step. The data in Fig V contain the result for ortho-nitrotoluene and para-nitrotoluene. These are carried out under conditions which are similar to that for the nitrobenzene studies. Our ortho-iodotoluene results demonstrate that toluene yields can be used as a measure of C-NO₂ bond cleavage in these systems. The comparative rate expressions for the three systems are,

$$\begin{aligned} \text{Log}k(\text{C}_6\text{H}_5\text{NO}_2 \rightarrow \text{C}_6\text{H}_5 + \text{NO}_2) &= (.937 \pm .005) \text{Log} k(1,2\text{DMC}) + (.756 \pm .01) \\ \text{Log}k(o\text{-CH}_3\text{C}_6\text{H}_4\text{NO}_2 \rightarrow o\text{-CH}_3\text{C}_6\text{H}_4 + \text{NO}_2) &= (.885 \pm .011) \text{Log}k(1,2\text{DMC}) + (1.229 \pm .017) \\ \text{Log}k(p\text{-CH}_3\text{C}_6\text{H}_4\text{NO}_2 \rightarrow p\text{-CH}_3\text{C}_6\text{H}_4 + \text{NO}_2) &= (.917 \pm .005) \text{Log}k(1,2\text{DMC}) + (.680 \pm .009) \end{aligned}$$

Figure VI contains data on experiments where ortho-nitrotoluene decomposition is compared to nitrobenzene decomposition. The comparative rate expression is

$$\text{Log}k(o\text{-CH}_3\text{C}_6\text{H}_4\text{NO}_2 \rightarrow o\text{-CH}_3\text{C}_6\text{H}_4 + \text{NO}_2) = (.926 \pm .015) \text{Log} k(\text{C}_6\text{H}_5\text{NO}_2 \rightarrow \text{C}_6\text{H}_5 + \text{NO}_2) + (.43 \pm .03)$$

Substituting into the first three relations the rate expression for 1,2 dimethylcyclohexene decomposition we obtain,

$$\begin{aligned}
 k(\text{C}_6\text{H}_5\text{NO}_2 \rightarrow \text{C}_6\text{H}_5 + \text{NO}_2) &= 1.9 \times 10^{15} \text{Exp}(-33026/T)/\text{s} \\
 k(o\text{-CH}_3\text{C}_6\text{H}_4\text{NO}_2 \rightarrow o\text{-CH}_3\text{C}_6\text{H}_4 + \text{NO}_2) &= 8.8 \times 10^{14} \text{Exp}(-31193/T)/\text{s} \\
 k(p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_3 \rightarrow o\text{-CH}_3\text{C}_6\text{H}_4 + \text{NO}_2) &= 7.7 \times 10^{14} \text{Exp}(-32305/T)/\text{s}
 \end{aligned}$$

If we now substitute into the fourth expression the rate expression given above for nitrobenzene decomposition we obtain,

$$k(o\text{-CH}_3\text{C}_6\text{H}_4\text{NO}_2 \rightarrow o\text{-CH}_3\text{C}_6\text{H}_4 + \text{NO}_2) = 4 \times 10^{14} \text{Exp}(-30582/T)/\text{s}$$

and thus represents a satisfactory check of the earlier results. Note that the rate constants at the reaction temperature are practically identical for the two cases. This is very important for ortho-nitrotoluene decomposition since it demonstrates that the unspecified main reactive channel does not release radicals with peculiar reactivity properties. For the present purpose our "best" rate expression will be the average of the two measurements or

$$k(o\text{-CH}_3\text{C}_6\text{H}_4\text{NO}_2 \rightarrow o\text{-CH}_3\text{C}_6\text{H}_4 + \text{NO}_2) = 6.4 \times 10^{14} \text{Exp}(-30888/T)/\text{s}$$

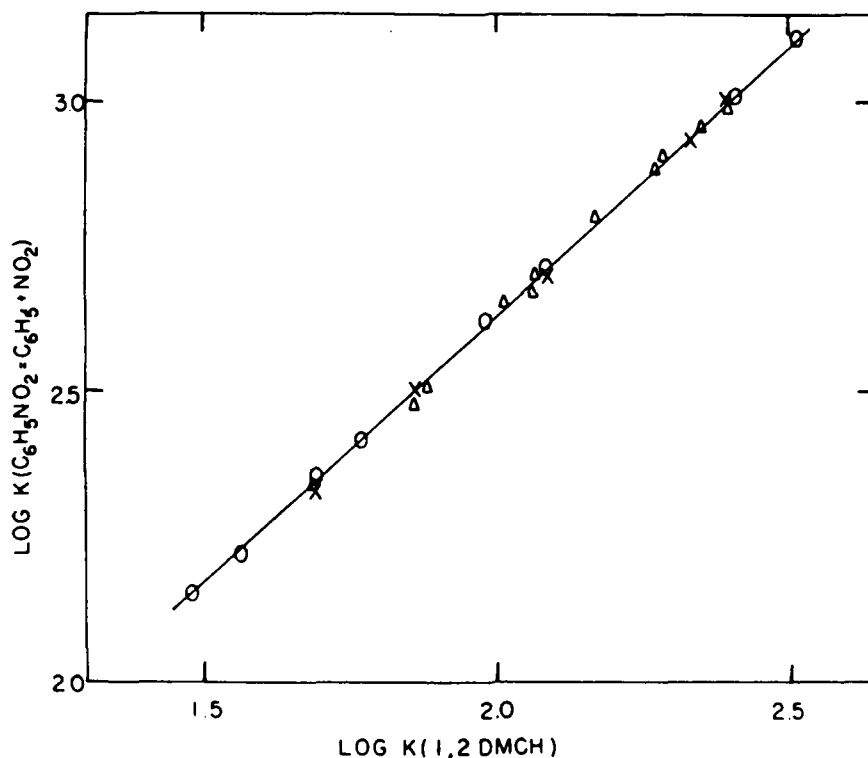


Figure IV: Comparative Rate Studies on the Breaking of the C-NO₂ bond in Nitrobenzene and 1,2 Dimethylcyclohexene (1,2DMCH) Decomposition,
 (O) 444 ppm Nitrobenzene, 879 ppm 1,2 Dimethylcyclohexene and 5.1% Cyclopentane in Argon
 (x) 111 ppm Nitrobenzene, 220 ppm 1,2 Dimethylcyclohexene and 1.3% Cyclopentane in Argon
 (Δ) 65 ppm Nitrobenzene, 129 ppm 1,2Dimethylcyclohexene and 5.2% Cyclopentane in Argon
 Pressure - 2 - 10 atms., Temperature - 1080 - 1160K

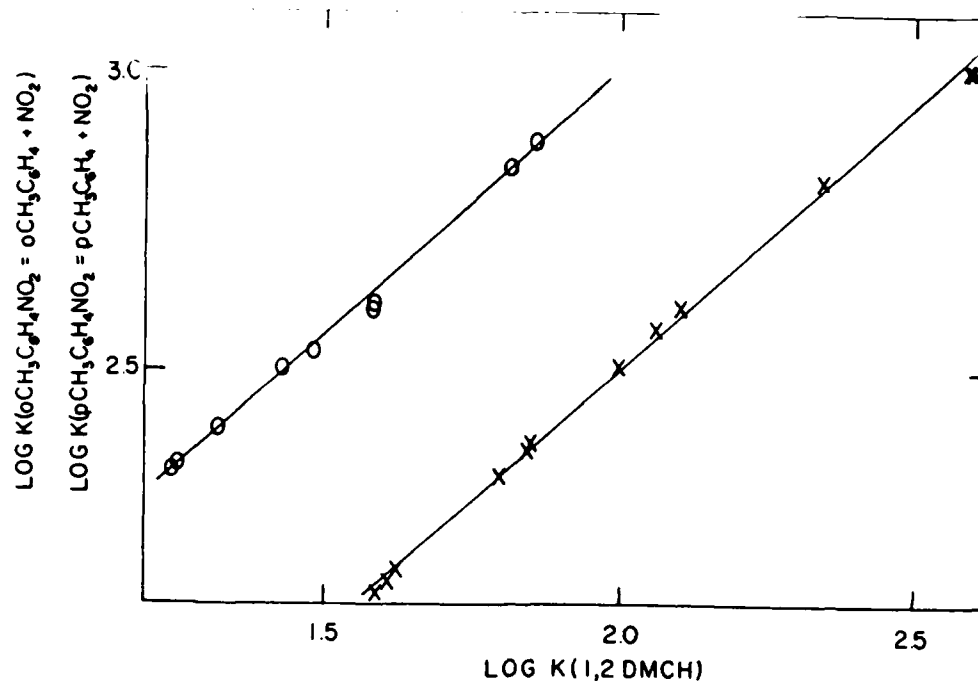


Figure V: Comparative Rate Studies on the Breaking of the C-NO₂ bond in o-Nitrobenzene, and p-Nitrobenzene and 1,2Dimethylcyclohexene Decomposition (O) 166 ppm o-Nitrotoluene and 647 ppm 1,2DMCH in 5.2% Cyclopentane and Argon (x) 148 ppm p-Nitrotoluene and 434 ppm 1,2 DMCH in 5.2% Cyclopentane and Argon Temperature = 1070 - 1180K; Pressure = 4 Atm.

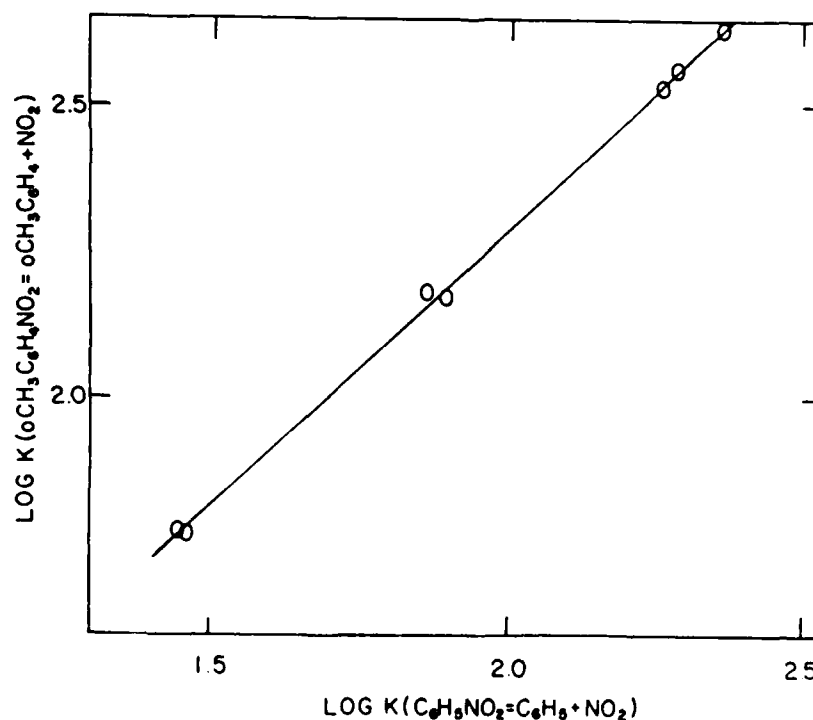
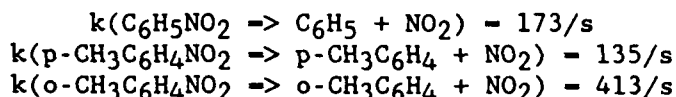


Figure VI: Comparative Rate Studies on the breaking of the C-NO₂ bond in Nitrobenzene and o-Nitrobenzene Decomposition, 164 ppm Nitrobenzene and 145 ppm o-Nitrobenzene in 5.2% Cyclopentane and Argon. Temperature= 1060-1120K, Pressure = 4 atm.

For nitrobenzene decomposition, we have varied the reaction pressure by a factor of four without any perceptible effect. Since 1,2 dimethylcyclohexene decomposition is at the high pressure limit(7) we conclude that the rate expression for nitrobenzene decomposition and by inference those of the other two larger compounds are high pressure limiting values. Finally, for subsequent comparisons our rate expressions at 1100K lead to,



Thus at 1100K, the relative rate ratio for the three compounds are 2.4:1:.78 for o-nitrotoluene, nitrobenzene and p-nitrotoluene respectively. In the case of nitrobenzene the results also suggest that the bond cleavage reaction is favored over the NO₂ isomerization process by at least 2 to 1. From the product distribution in para-nitrotoluene decomposition the inference is very strong that this is also the case. In ortho-nitrotoluene decomposition, the main reaction is still undetermined. At these temperatures, it is about two times more important than the C-NO₂ bond breaking process and a factor of 5 faster than the isomerization reaction.

5.4 Discussion: The experimental results presented above illustrates the "rich" chemistry that characterizes nitroaromatic decomposition. In the case of nitrobenzene and para-nitrotoluene, under our reaction conditions, there are at least two important initial decomposition channels, C-NO₂ bond cleavage and C-NO₂ isomerization to form the nitrite prior to the breaking of the O-NO bond. For ortho-nitrotoluene there remains another as yet undefined process which represents the primary decomposition channel.

At the present time definitive quantitative conclusions can only be reached with respect to the C-NO₂ bond cleavage. The rate expressions represent essentially local properties and are not strongly effected by substitution at the neighboring sites. Nevertheless it is interesting to note the factor of 2.4 increase in rate of C-NO₂ bond cleavage by methyl substitution at the ortho site contrasts strongly with the virtual absence of any effect on C-I bond cleavage in a similar situation. The 20% decrease in rate arising from methyl substitution at the para-site is not much above the experimental uncertainty. These small effects may well be a reflection of the changes in the stability of the parent molecule. This is the conclusion of Barton and Stein(24) for the effect of methyl substitution on the rate of decomposition of ethyl benzenes and substituted pyridines. In the present case there are not any thermodynamic data on the nitrotoluenes to test this hypothesis.

The measured A-factors for C-NO₂ bond cleavage are very close to those for aromatic iodine compounds that we have previously studied. This is somewhat surprising since with the additional rotational degrees of freedom which are not available to an atom one would expect a considerably larger A-factor. This is suggestive of a slower than expected combination rate for phenyl + NO₂. These considerations can be placed on a quantitative basis using the thermodynamic properties of these species and detail balancing. If one assumes a combination rate that is independent of temperature, then a value for the heat of formation of phenyl radicals can be derived. Unfortunately,

thermodynamic functions of nitrobenzene have never been tabulated. We have accordingly derived our own set of values using as a basis the heat of formation of nitrobenzene of 67.36 kJ/mol(300K) as given in Pedley et al.(25) and the vibrational assignment of Green and Harrison(26). Combining this with the thermodynamic functions of phenyl radical as tabulated by Burcat et al(16) gives a rate expression for the combination of phenyl + NO₂ of 3.7×10^{81} l/mol-s over our temperature range. This is based on a heat of formation of phenyl of 328.5 kJ/mol(300K). Using our recently derived higher value of 340 ± 10 kJ/mol from phenyl iodide decomposition we obtain a rate constant for combination of 1.2×10^{91} l/mol-s at 1100K with a 1/T temperature dependence. Regardless of the spread of the results, our data is indicative of a "slow" combination rate. The combination of phenyl and NO₂ can lead to the formation of the nitrite as well as the nitro compound. Thus the usual "loose" complex picture of radical combination with radicals tumbling about each with only steric constraints must be modified in order to take into account the other possible reaction channel. Note however, from detail balancing and our study on iodobenzene decomposition, we obtained a value for phenyl + I of between 5 to 15×10^9 l/mol-sec. This is also lower than what one would commonly expect for the combination of a radical and an atom.

Our results do permit some estimate to be made of the rate expressions for the non-bond breaking processes. In the case of isomerization to the nitrite our nitrobenzene results suggest a branching ratio of more than 2 to 1 in favor of bond breaking. Assigning a normal A-factor of 1×10^{13} /s or a value similar to that for methyl isocyanide isomerization, we obtain an activation energy of no less than 234 kJ/mol. Similarly, for our undefined main reaction in orthonitrotoluene decomposition a $1 \times 10^{12+1}$ /s A-factor will lead to an activation energy of 194 ± 20 kJ. As will be seen subsequently our estimate is in very good agreement with the direct measurement to be described below.

6. Formation and Destruction of Anthranil in o-Nitrotoluene Decomposition

6.1 Experimental: Except for the gas chromatography the experimental procedure was similar to that used in the earlier experiments. Analysis of the products was by capillary gas chromatography using a 60 meter bonded methyl, phenyl and vinyl silicone capillary column. Detection is by hydrogen flame ionization. With such a column very detailed analysis of the higher boiling components can be made. We give up information on the light hydrocarbons. However, we have reported on them in detail in the earlier study. Furthermore, in this and the earlier study yields of toluene are given and thus serves as a bridge for linking the two sets of data.

Our results are based primarily on studies on two mixtures, 285 ppm o-nitrotoluene in 4.81% cyclopentane and argon and 182 ppm anthranil, and 84 ppm p-nitrotoluene in 4.97% cyclopentane and argon. Ancillary experiments are also carried out to verify various aspects of the reaction mechanism. The anthranil and o-nitrotoluene have been obtained from Aldrich Chemicals. The cyclopentane is from Wiley Organics and the Argon is of Research Purity and is from Matheson. Except for vigorous degassing of the organics all of the substances are used without further purification. Anthranil samples showed some instability over the period of days during which we carried out our experiments. However, they did not lead to any new detectable products and the results of experiments over different

periods of time are reproducible.

6.2 Results: Figure VII gives the product distribution from the gas chromatographic analysis of the mixtures obtained from shocking dilute solutions of o-nitrotoluene in cyclopentane. As noted earlier, with our column we lose information on the light hydrocarbon products. Also, with such excesses of cyclopentane as we have in this system the first of the heavier compounds that we can reliably quantify is toluene. Also present in small amounts are compounds such as picoline, aniline and diazobenzene. Except for the anthranil, the compounds listed in Figure VII are the major large hydrocarbon products. Anthranil is present in extremely small quantities. The reason for its inclusion will become clear subsequently. In exactly, the same experiments with p-

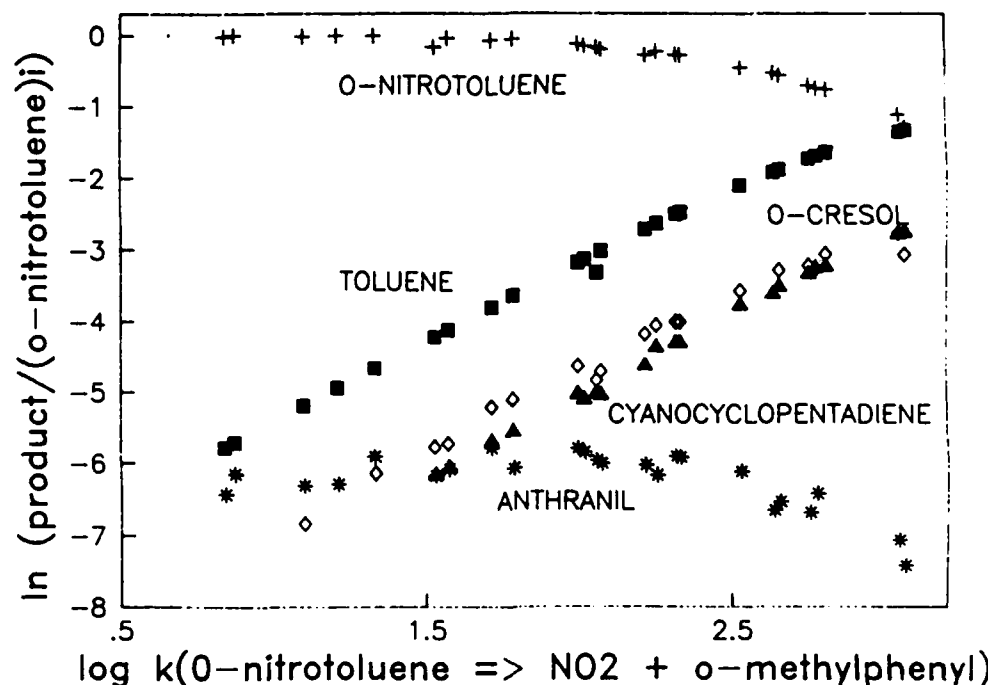


Figure VII: Higher Molecular Weight Fragments from the Decomposition of o-Nitrotoluene. 285 ppm o-Nitrotoluene in 4.85% Cyclopentane and Argon. 2-4 atms., Pressure. 1000 - 1170K Temperature.

nitrotoluene we confirmed our earlier results with regard to the recovery of close to 70% of the product as toluene and 10-15% as p-cresol. No anthranil or cyanocyclopentadiene could be detected.

The presence of all of the compounds except for cyanocyclopentadiene have been verified with neat samples. We have not been able to purchase this compound. Our assignment is based on the fact that it is the expected final product from the decomposition of anthranil and this was in fact verified directly. Furthermore, in the hydrogen atom induced decomposition of aniline we identified large yields of compounds in this region. We have attempted to generate cyanocyclopentadiene from benzentriazole, a standard source. Unfortunately, the compound did not survive storage in our mixing vessel. Actually, for our present

purposes the nature of the peak that we assigned to cyanocyclopentadiene is not important since all that we really need is to establish that this peak is also formed in the decomposition of anthranil. This was carried out in experiments with only anthranil and in the presence of cyclopentane. However, although virtually total destruction of anthranil was easily achieved, under all conditions of these experiments > 800 K, it was not until the highest temperatures that we recovered over 50% of the decomposed anthranil and at the lowest temperatures yields of the cyanocyclopentadiene was as low as 5%. This suggests that we should be able to determine the quantity of anthranil initially formed in o-nitrotoluene decomposition on the basis of the cyanocyclopentadiene that is detected. We therefore carried out studies on anthranil decomposition in the presence of p-nitrotoluene and determine the ratio of anthranil destroyed (virtually all that was introduced) to cyclopentadiene found using the formation of toluene from p-nitrotoluene

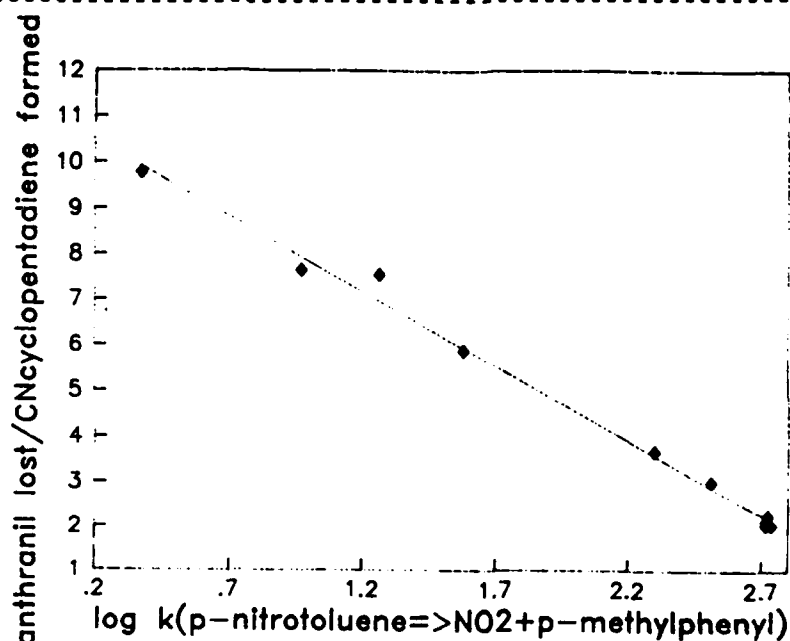


Figure VIII: Ratio of the Amount of Anthranil Disappeared and Cyanocyclopentadiene Formed as a Function of Reaction Conditions during Anthranil Decomposition. 185 ppm Anthranil, 85 ppm p-Nitrobenzene in 4.91% Cyclopentane and Argon 2-4 Atms., Pressure. 1000-1150K, Temperature.

decomposition as the internal standard to define the reaction temperature. The rate expression for the latter is

$$k(p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_3 \rightarrow \text{NO}_2 + p\text{-CH}_3\text{C}_6\text{H}_4) = 7.7 \times 10^{14} \text{ Exp}(-32305/T)$$

The results can be found in Figure VIII. We will use this data as a calibration curve and deduce the quantities of anthranil that must be initially present on this basis.

With this result we can now return to the data in Figure VII and deduce from the

cyanocyclopentadiene yields the rate expression for anthranil formation in o-nitrotoluene decomposition. For this purpose we make use of the rate expression that we have previously derived for o-nitrotoluene decomposition,

$$k(o\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_3 \rightarrow \text{NO}_2 + \text{C}_6\text{H}_5\text{CH}_3) = 6.4 \times 10^{14} \text{ Exp}(-30888/T)/s$$

as the internal standard and convert the data on anthranil decomposition to the same basis by making use of the two rate expressions given above. In making this correction we have also taken into account of the fact that in the experiments summarized in Figure VII, the anthranil is generated throughout the reaction period. On the other hand, in the experiments with anthranil itself all of it is present initially. Measured destruction rates will be correspondingly greater. We have taken this into account by multiplying the anthranil to cyanocyclopentadiene ratio in Figure II by a factor of 2. The corrected anthranil concentrations, representing the quantity that is initially formed but which subsequently decomposed ranged from a factor of 5 to 20 times higher than the cyanocyclopentadiene detected.

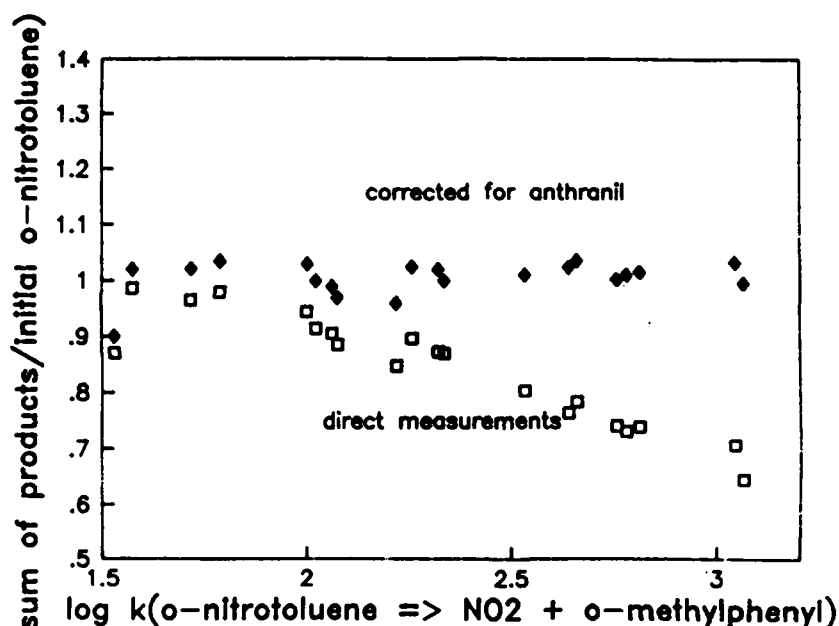


Figure IX: Test of Mass Balance in o-Nitrotoluene Decomposition. 285 ppm o-Nitrotoluene in 4.81% Cyclopentane and Argon. 2-4 Atms., Pressure. 1000-1170K Temperature.

Figure IX demonstrate the situation with respect to mass balance. It can be seen that with the correction made above the products include all the reactants that have disappeared. In contrast we also display the situation when we make use of only the directly measured values where the mass balance is very poor. Note that at the lower rate constants for o-nitrotoluene, the low conversions makes it difficult to make proper mass balances. A major problem in single pulse shock tube experiments is the inability to vary reaction time. Thus the data for low

extent of reactions are really only a measure of the accuracy of our chromatographic measurements on the nitrotoluene.

On this basis we can now calculate the relative rates for the production of anthranil and o-methylphenyl radicals. The rate constants can be calculated from the relations.

$$k(o\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_3 \rightarrow \text{NO}_2 + \text{C}_6\text{H}_5\text{CH}_3) = \log(1 - (\text{toluene} * X / o\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_3)) / t * X$$

and $k(o\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_3 \rightarrow \text{NO}_2 + \text{C}_6\text{H}_5\text{CH}_3) / k(o\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_3 \rightarrow \text{anthranil}) = \text{toluene} / \text{anthranil}_c$

where t is the residence time and is of the order of 450 microsecs, X is the factor that takes into account the none C-NO₂ cleavage channels in o-nitrotoluene decomposition and anthranil_c is the corrected anthranil concentration. The comparative rate plot can be found in Figure X and the relation between the two reaction channels have been found to be

$$\log(k(o\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_3 \rightarrow \text{NO}_2 + \text{C}_6\text{H}_5\text{CH}_3)) = (.843 \pm .017) \log(k(o\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_3 \rightarrow \text{anthranil})) + (.598 \pm .039)$$

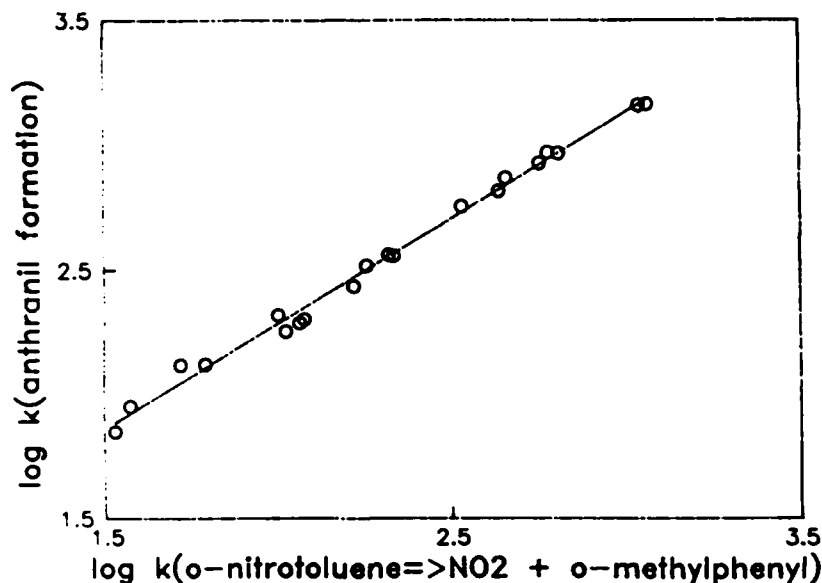


Figure X: Comparative Rate Plot for the Breaking of the C-NO₂ Bond and Anthranil formation during o-Nitrotoluene Decomposition. 285 ppm o-Nitrotoluene in 4.81% Cyclopentane and Argon. 2-4 Atms., Pressure. 1000-1170K Temperature.

Substituting into the above the rate expression for the breaking of the C-NO₂ bond in o-nitrotoluene, we find

$$k(o\text{-nitrotoluene} \rightarrow \text{anthranil} + \text{H}_2\text{O}) = 1.2 \times 10^{13} \text{ Exp}(-26038/T) / \text{s}$$

Note that as written this is not an elementary single step reaction. In a

subsequent section, we will however identify this rate expression with an particular process.

We have also included in Figure VII the yields of anthranil as a function of the extent of reaction. It can be seen that the yields are very small. This is due to the relative instability of the anthranil in our system. It is thus possible to assume that steady state for anthranil is achieved. Thus the formation and decomposition of anthranil as represented by the subscripts f and d can be related as follows

$$k(\text{anthranil})_d / k(\text{anthranil})_f = (\text{o-nitrotoluene})_i * \text{Exp}(-k(\text{o-nitrotoluene}) * t) / (\text{anthranil})$$

where $k(\text{o-nitrotoluene})$ can be expressed as the sum of the three modes of decomposition, C-NO₂ bond cleavage, NO₂ isomerization to form the nitrite and anthranil formation, t is the residence time of approximately 450 microsecs and $(\text{o-nitrotoluene})_i$ is the initial concentration. On this basis we obtain the comparative rate plot as given in Figure XI relating anthranil decomposition with C-NO₂ bond cleavage in o-nitrotoluene decomposition. The comparative rate expression is then

$$\log k(\text{anthranil})_d = (.840 \pm .038) \log (k(\text{o-NO}_2\text{C}_6\text{H}_4\text{CH}_3 \rightarrow \text{NO}_2 + \text{C}_6\text{H}_5\text{CH}_3)) + (3.130 \pm .088)$$

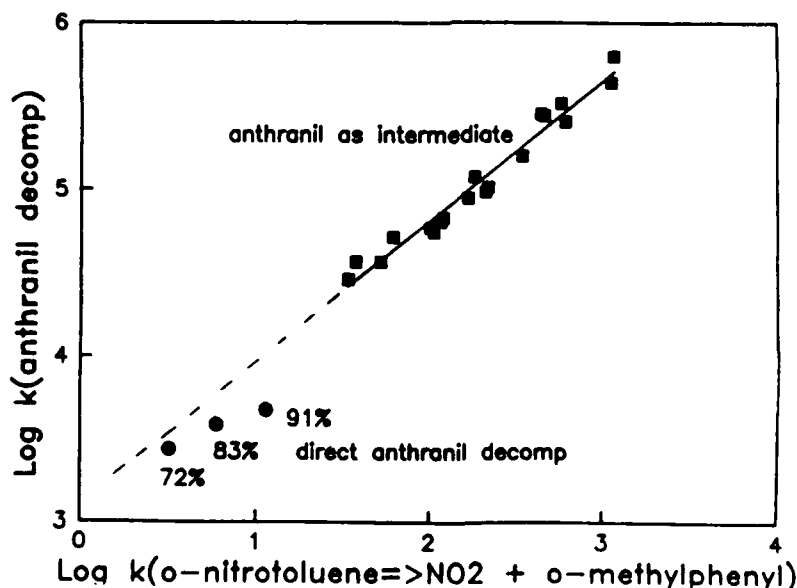


Figure XI: Comparative Rate Study on the Decomposition of Anthranil and the Breaking of the C-NO₂ bond in o-Nitrotoluene Decomposition. Studies with Anthranil as Intermediate 285 ppm o-Nitrobenzene in 4.81% Cyclopentane. Anthranil Decomposition Study with 100 ppm o-Nitrobenzene and 700 ppm Anthranil in 6% Cyclopentane and Argon. 2-4 Atm., Pressure. 900 -1170K, Temperature. Percentage refers to anthranil decomposed.

and this leads to the rate expression;

$$k(\text{anthranil})_d = 3.7 \times 10^{15} \text{ Exp}(-25945/T)/s$$

The comparative rate data show considerable scatter. This is a reflection of the derivative nature of the determination and the very low yields of anthranil that was detected. Unlike the situation with respect to anthranil formation, we will show subsequently that it is relatively easy to assign this rate expression to the breaking of the N-O bond in anthranil. Also included in Figure XI are data from comparative rate studies with anthranil and o-nitrotoluene. The anthranil is present in sufficiently large concentrations so that the small amount produced in o-nitrotoluene decomposition does not make any contributions. The experiments are rendered difficult by the great differences in stability between the two compounds. Practically all the anthranil will have disappeared before o-nitrotoluene starts to decompose. Fortunately we are able to carry out a few experiments that are meaningful. It can be seen that our extrapolated rate expression passes very close to the point where there is the lowest extent of decomposition. At the higher decomposition ranges the discrepancy becomes more serious. This is completely understandable in terms of the anthranil that is in the boundary layer and is thus not heated. This has been observed by other workers(27). The present results is thus a fine consistency check of our rate expression for anthranil decomposition. Indeed, if we just use our lowest extent of reaction as a fixed point and estimate the A-factor by thermokinetic considerations we would obtain a rate expression very similar to that which we determined here. We can then reverse the process and derive the rate expression for anthranil formation without recourse to the quantity of cyanocyclopentadiene that we measured.

6.3 Discussion: The results of our study show that under our experimental conditions there are three modes for the decomposition of o-nitrotoluene. The most important of these channels involves anthranil formation and is specific with respect to the presence of the methyl group adjacent to the NO₂ moiety. The low activation energy for this process means that at lower temperatures this will be an even more important process. We have noted earlier that our rate expression certainly does not represent the direct process of anthranil formation. Undoubtedly a number of reaction processes are involved. The A-factor suggest a relatively tight complex and it would appear that a retroene reaction involving hydrogen atom transfer would not be incompatible with our results. Indeed our rate expression is very much in line with other such processes(28). Figure XII represents a possible sequence of reactions that can lead to anthranil formation from o-nitrobenzene decomposition. It should be noted as with the retroene reaction all of the listed processes has ample precedents. An important question is the nature of the secondary reactions. Is there a mechanism for the direct formation of the anthranil from the acid through the ejection of water? Or is there as sequential series of reactions which releases OH and the H-atoms in the system. We do note from our earlier study the increased yields of light hydrocarbons from that which can be expected purely on the basis of o-phenylmethyl and NO₂ radicals released into the system.

The rate expression for the decomposition of anthranil is reflective of the breaking of the -N-O- bond. The activation energy is somewhat lower than that for

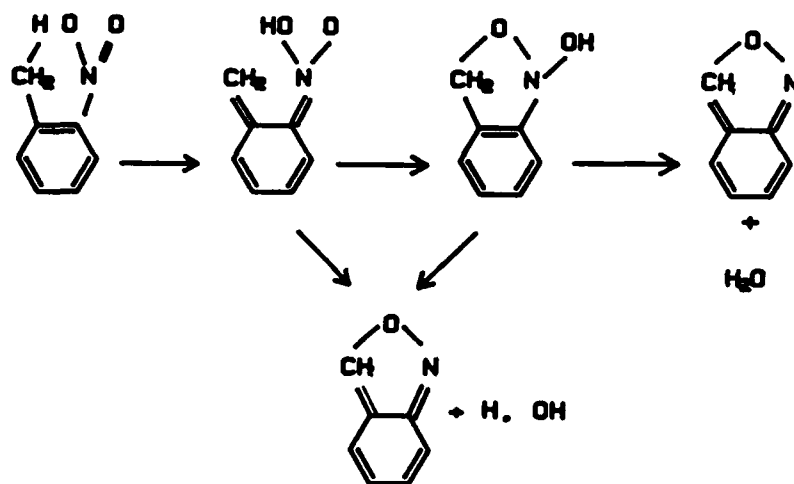


Figure XII: Possible Mechanisms for the Formation of Anthranil during o-Nitrotoluene Decomposition

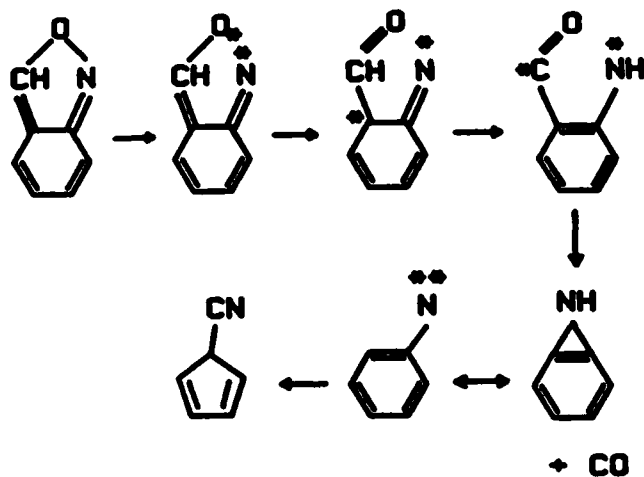


Figure XIII. Possible Reaction Mechanism for Anthranil Decomposition and Cyanocyclopentadiene Formation.

the decomposition of an oxime. The larger than "normal" A-factor is in line with the increased entropy in the activation energy as a result of the loosening of the more rigid stable ring structure. It can be assumed that the subsequent reactions will follow the sequence of processes as outlined in Figure XIII

These results have important implications on the nature of the initial process in the decomposition of trinitrotoluene. Certainly, it is no longer possible to assume that it involves C-NO₂ bond cleavage. Instead all evidence point to a sequence of reactions during which anthranil is an important reaction intermediate. Note that since our reaction temperature is well above ignition temperatures for trinitrotoluene, the smaller rate parameters for the anthranil decomposition channel means that it will be even more dominant at the lower temperatures. In addition the fact that the decomposition of o-nitrotoluene to anthralinic acid (29) at lower temperatures is supposed to proceed via an anthranil intermediate(30,31) and is base-catalyzed provides an alternative channel for anthranil formation. This line of argument is supported by the detection by Dakons and coworkers(5) of significant quantities of di-nitroanthranil in trinitrotoluene decomposition. Clearly, future work must concentrate on the details of how it is formed and the mechanism for destruction. A particularly interesting question is whether the addition of another nitro group will drastically change the rate constants. We are planning to carry out such experiments in the near future.

7. Comparison with Laser Pyrolysis Studies:

The laser pyrolysis study of Gonzalez and coworkers(6) show considerable discrepancies from our results. These can be inferred from a comparison of the rate constants and expressions that we have presented earlier and the data in Table I. In the case of nitrobenzene the rate constants at 1100K are within a factor of two of each other and the rate expressions are in essential agreement. However in all other cases there are gross disagreements. Note that their stated reaction pressure is a factor of 10 lower than ours. Thus the corrections that they have made for falloff effects are quite appropriate. In the case of ortho-nitrotoluene they report 75% recovery of their products as toluene. We recover no more than half of this amount. Their rate constants for ortho-nitrotoluene decomposition is approximately a factor of 3 higher than ours. For para-nitrotoluene decomposition, they obtained rate constants that are approximately a factor of 5 lower than ours. Thus their results lead to much larger effects for methyl substitution on the ring. They find the result on the rate constants for C-NO₂ bond cleavage of moving a methyl group from the ortho to the para position is a decrease of a factor of 50 as against our factor of 3. It should be emphasized that these effects are occurring at temperatures of 1100K. Thus a factor of 50 is equivalent to an activation energy difference of 40kJ/mol or an entropy of activation difference of 33J/mol-K. These appear to us to be remarkably large quantities. In contrast Barton and Stein(24) have found that methyl substitution at various positions on the ring have at most factors of 2 effects on rates of benzyl C-C bond cleavage in substituted ethylbenzene. Similarly, in our study of ortho-iodotoluene and iodobenzene(8) rate constants are virtually equal.

We are unaware of the cause of these serious discrepancies. Particularly distressing is the non systematic nature of the differences. Thus a number of

simple explanations are immediately eliminated. We suspect that there is a need to more closely define the conditions in the laser experiments. In contrast to the well defined heating pulse in the shock tube experiments the exact nature of the laser induced pulse is very uncertain. The pressure, temperature and time scale of the experiments are poorly defined. It is thus possible that the actual temperatures achieved in the laser pulse are much higher than the 1000-1100K claimed by Gonzalez and coworkers(6). Indeed, we have been informed by McMillen and Golden that their mass balance studies are carried out under temperatures and reaction extents much higher than that used in determining their rate expressions. This may provide a rationale for the different product distribution in orthonitrotoluene decomposition. If the higher temperatures is accompanied by higher pressures than it may be possible to account for the very successful scavenging of phenyl radicals. We note that with the stated conditions in the laser heating experiments and reasonable abstraction rate constants for phenyl radical attack on the scavenger complete conversion to toluene cannot be expected. This can be inferred from the data in Table II. There the conditions under which we are no longer able to scavenge all the phenyl radicals are in fact more favorable for such processes than under laser pyrolysis. Also note from Table VI our failure to achieve as large conversions to toluene using o-fluorotoluene(the scavenger used by Gonzales and coworkers(6)) as with cyclopentane during o-nitrotoluene decomposition.

It should be noted that although the internal standard technique is extraordinarily forgiving with respect to uncertain reaction conditions, the enormous gradients in time and space in the laser experiments can lead to significantly large errors in relative rates (factors of 2 or 3) even for differences as small as 5% in activation energies. Since the single pulse shock tube technique is well established and the findings from such studies have been repeatedly verified, the present results indicate the need of caution in the quantitative interpretation of laser heating experiments. In the case of o-nitrotoluene decomposition our results lead to a difference of 40 kJ in activation energy between the two channels. In order to arrive at the 75% product recovery in the laser experiments we need temperatures as high as 1700K. This seems extraordinarily high, although if one takes into account possible uncertainties this can be easily reduced to 1500K. Nevertheless, aside from experimental artifacts no alternative explanation is possible. In any case we believe that this kind of direct comparisons can play a valuable role in properly defining exactly what is happening during laser heating.

PARTICIPATING SCIENTIFIC PERSONNEL

The following staff contributed to this project

W. Tsang

W. G. Mallard

D. Robaugh

Y. Z. He

J. P. Cui

LIST OF PUBLICATIONS

1. D. Robaugh and W. Tsang, "Thermal Decomposition of Phenyl iodide and o-Iodotoluene, J. Phys. Chem., in press (Sept, 1986)
2. W. Tsang, D. Robaugh and W. G. Mallard, " Single Pulse Shock Tube Studies on C-NO₂ Bond Cleavage During the Decomposition of Some Nitro Aromatic Compounds" J. Phys. Chem., in press (October, 1986)
3. Y. Z. He, J. P. Cui, W. G. Mallard and W. Tsang, " Homogeneous Gas Phase Formation and Destruction of Anthranil During o-Nitrotoluene Decomposition" in preparation

Summary

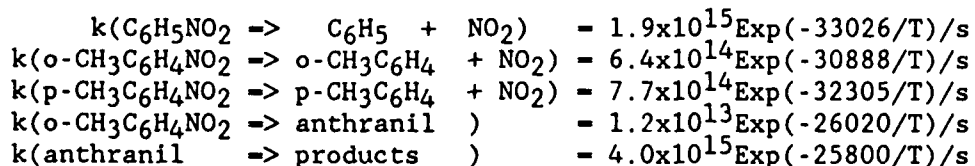
Rates and mechanisms of the thermal decomposition of nitrobenzene, o-nitrotoluene, p-nitrotoluene, iodobenzene, o-iodotoluene and anthranil have been studied in single pulse shock tube experiments. The first three compounds are of direct interest. They can be regarded as prototypical of the nitroaromatic explosives and as such have been of continuing interest to kineticists. The iodobenzene and o-iodotoluene systems were studied in order to establish the conditions under which every phenyl and methylphenyl radical is trapped as benzene during our experiments. It was necessary to study anthranil decomposition because this compound proved to be the major product in o-nitrotoluene decomposition.

The main channel for the decomposition of nitrobenzene and p-nitrotoluene is C-NO₂ bond cleavage. A minor channel involving NO₂ isomerization to the nitrite proceeds at about one-half to one-third the rate. o-Nitrotoluene decomposition led to results that proved to be surprising. C-NO₂ bond cleavage and NO₂ isomerization contributed to less than half of the total decomposition process. From careful analysis of the nature of the decomposition products we find the main reaction channel involve the relatively unstable compound, anthranil. The latter rapidly decomposes under our conditions and the major pathways has been identified as the formation of a nitrene and then cyano-cyclopentadiene.

Comparative rate experiments are carried out to obtain accurate rate expressions. For this purpose we used as an internal standard the reverse Diels-Alder decomposition of 1,2 dimethylcyclohexene(1,2DMC) to form ethylene and 2,3

$$k(1,2DMC) = 10^{15.5} \text{Exp}(-34800/T)/s$$

This then led to the following rate expression for the decomposition of the nitroaromatic and related compounds;



In addition, we estimate that the rate expression for the isomerization of the nitro compounds to the nitrite is approximately $10^{13} \text{Exp}(-27600/T)/s$.

The general trend of these rate expressions are in accord with expectations. It can be seen that the A-factors for C-NO₂ bond breaking are very close to each other. This is to be expected since the transition state structure for such similar processes should not vary greatly. In conjunction with the thermochemistry we obtain a combination rate between phenyl type radicals and NO₂ of approximately 10^9 l/mol-s. This is somewhat lower than combination rates involving organic radicals and may be due to the possibility of nitrite formation as an alternative reaction channel. The relative rate constants for C-NO₂ bond breaking are of the order of 2.4:1:8 for nitrotoluene: nitrobenzene: p-nitrobenzene at the reaction temperature of approximately 1050K. Thus the effect of methyl substitution on the ring for C-NO₂ bond cleavage is seen to be relatively small under our conditions. The degradation of o-nitrotoluene

ultimately to form anthranil is characterized by a relatively small pre-exponential factor. This is indicative of a concerted process similar to the retro-ene reactions that we are familiar with in hydrocarbon chemistry. In the course of conversion to anthranil channels leading to OH and H atom production and H₂O formation make contributions. The relatively large A-factor for anthranil decomposition is in line with the large entropy of activation to be expected with the breaking of the five membered ring.

The conclusion to be drawn from these studies is that the methyl grouping ortho to the nitro moiety leads to the opening of a new preferred reactive channel. This pathway releases radicals into the system. At temperatures lower than that utilized here, where ignition of nitroaromatic explosives occurs, this will be the strongly preferred in comparison to simple C-NO₂ bond cleavage finally, we compare our results from recent studies using laser pyrolysis and find disturbing differences. It is suggested that the conditions for such experiments need to be better defined.

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