# Kinetics and Mechanisms of Thermal Decomposition of Nitroaromatic Explosives

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*Received February 23, 1993 (Revised Manuscript Received August 19, 1993)*

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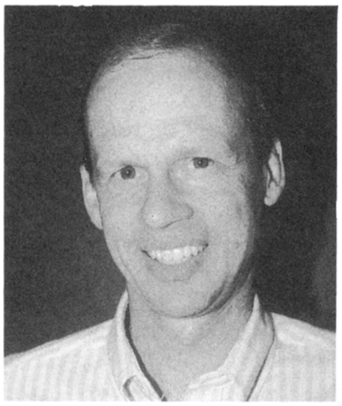
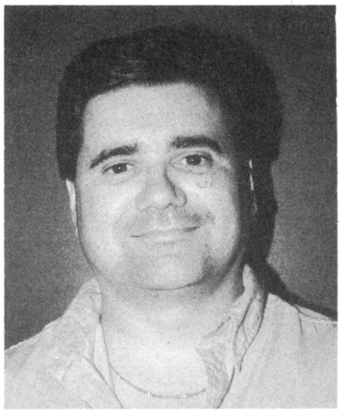
## *I. Introduction*

No critical review exists of the thermal decomposition mechanisms of polynitroaromatic explosives. This void is surprising in view of the fact that 2,4,6-trinitrotoluene (TNT) has been available as a pure material since about 1870 and is very widely used. For any explosive the thermal decomposition mechanisms and resultant products are important details because they guide systematic predictions about unknown explosive molecules, influence feasibility of large-scale synthesis, predict long-term stability for purposes of storage, and predict sensitivity to various stimuli, such as heat and mechanical impact. Although safety and performance of explosives are intimately tied to the thermal decomposition process, knowledge of the mechanisms does not automatically lead to improvement in safety and performance. However, without mechanistic information, the behavior of explosives remains disconcertingly empirical.



Thomas B. Brill was born in 1944 in Chattanooga, TN, and was raised in Webster Groves, MO. He received his B.S. degree in 1966 with High Honors from the University of Montana. After completing his Ph.D. degree in 1970 from the University of Minnesota as an NDEA Fellow, he joined the University of Delaware in 1970 as Assistant Professor. He became full professor in 1979. His research interests have evolved from physical inorganic and organometallic chemistry in the 1970s to spectroscopy of rapid thermal decomposition mechanisms of energetic materials and reactions in supercritical water in the 1980s and 1990s.



Kenneth J. James was born in Woodstown, NJ, in 1962. He received his B.S. degree at the University of Delaware in 1984 and worked for Du Pont in the Clinical Chemistry Division and for Wilmington Chemical Corporation during 1984–1988. In 1988 he returned to the University of Delaware and is a Ph.D. candidate working in Professor Brill's laboratory.

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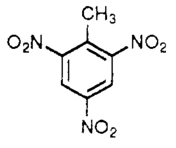
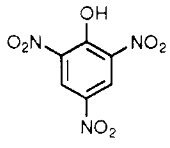
0009-2665/93/0793-2667$12.00/0

Robertson and Yoffe[1] and Wenograd[2] were among the earliest to connect thermal decomposition processes to initiation phenomena. Moreover, the thermal decomposition mechanisms and products are believed to influence the performance of the explosive, such as the Chapman–Jouguet (C–J) pressure (the pressure at the rear of the reaction zone of the detonation front) and the detonation velocity. For example Cook *et al.*[3,4] proposed that the initial reaction kinetics were important in determining the detonation velocity. Zeman and co-workers expanded this notion by attempting to correlate the thermal decomposition kinetics of polynitroaromatic explosives at lower temperature with molecular structure,[5] heat of explosion,[6] detonation characteristics,[5,7] and thermal stability.[8] The critical temperature of a thermal explosion is related to Arrhenius kinetics by the Frank-Kamenetskii model.[9-12]

A very large number of polynitrobenzene derivatives are known. All reasonable trinitrobenzene derivatives will explode if subjected to an energy input exceeding a threshold value. TNT achieves its special position because of its compatibility with other materials, low hygroscopicity, low melting point, low cost, relatively low sensitivity to impact and friction, good thermal stability. and high power during explosion. These characteristics influenced the German Army to adopt TNT in place of picric acid (PA), which is more hygroscopic, chemically reactive toward metals, and sensitive to impact. Other nitrobenzene derivatives having practical value as explosives are triaminotrinitrobenzene (TATB), 2,4,6-(trinitrophenyl)methylnitramine (Tetryl), hexanitrostilbene (HNS), and 1,3,7,9-6*H*-benzotriazolo[2,1-*a*]benzotriazol-5-ium (TACOT), which is used in two isomeric forms, Z and T, that differ in the position of the $-NO_2$ groups on the rings and the arrangement of the heterocyclic nucleus. Z-TACOT is shown. TATB has excellent thermal stability and is especially noteworthy for its extreme insensitivity to impact, shock, and transition from deflagration to detonation. Likewise, TACOT has exceptional thermal stability. It is able to retain predictable explosive characteristics after 10 min at 350 °C making it useful for deep-well oil exploration. Meyer[13a] is a good source of practical aspects of explosives.


TNT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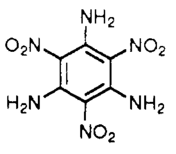
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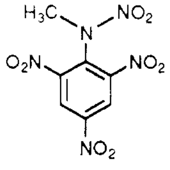
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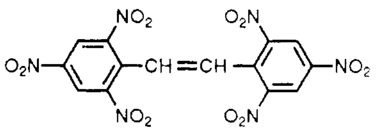
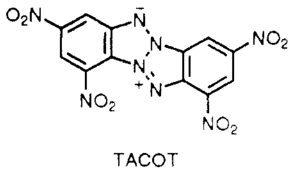

HNS


TACOT

A large amount of work has been conducted on decomposition processes of polynitroaromatics. Of the many conclusions reached, some are contradictory, many are perplexing, some are in unavailable government documents, and others are in untranslated, poorly circulated (at least in the United States) Russian literature. This article is an attempt to assess critically the literature of decomposition processes of polynitroaromatic compounds and to come to some conclusions about the dominant thermal mechanisms, especially in the bulk condensed phase where they begin to react as explosives.

First, it is necessary to outline why thermal decomposition mechanisms of explosives have produced divergent literature. Treacheries of the materials aside, the complications and realities of thermolysis processes of relatively large molecules in their bulk state and the restrictions on measurements are highlighted next in section II, parts A–D.

## *II. Special Considerations of Explosive Decomposition Chemistry*

The results and, ultimately, the description of thermal decomposition of an explosive depend on the amount and configuration of the sample, the rate and magnitude of energy loading, the diagnostics employed, and the interpretative scheme. Experimental conditions are frequently dramatically different from one laboratory to another which complicates comparison of the data.

### A. Dependence of Decomposition on the Conditions of Thermal Stimulus

Each of the many decomposition reactions of a complex organic molecule in the bulk condensed phase has a rate constant and sensitivity to temperature. The temperature to which the bulk material is heated and the heating rate control the time that the products from these reactions have to form. At lower temperatures, processes with lower activation energies and greater exothermicity are favored. Time is available for stable products to grow in concentration via the complex reaction network and to serve as catalysts. At higher temperatures, the higher activation energy and more endothermic processes increase in importance. However, the products have a shorter time to form and may or may not be the same as products formed at lower temperature. At least the product distribution will be different. Consequently, descriptions of decomposition processes depend significantly on the temperature and the heating rate, a fact that has led to many contradictory assertions. Aside from the chemistry, the physical details about the material, such as its thermal conductivity, heat capacity, hardness, void volume, void size, etc., contribute to the details of the decomposition process, especially during mechanical stress.[13b] The conversion of mechanical energy into chemical effects[14] is being addressed at an increasingly sophisticated level.[15-19]

### *1. Low Heating Rate/Low Temperature*

Programmed heating over minutes or hours to a chosen temperature while monitoring the change of heat flow or pressure is the basis of differential scanning calorimetry (DSC), differential thermal analysis (DTA), and manometry. The extracted decomposition rates tend to apply to the lower activation energy processes and reflect the overall (global) process, rather than a particular step. Zeman and co-workers[5–8] claim that correlations exist between the activation energies during the induction period before autocatalysis takes over and detonation properties pertaining to high pressure and temperature, such as the heat of explosion,[6] C–J pressure, and detonation velocity.[7] They suggest that the rate of early decomposition process is extendable to high temperature and pressure conditions. The products that are isolated by solvent extraction of TNT heated to a temperature characteristic of slow decomposition are numerous and frequently difficult to identify.[20,21]

### *2. Moderate Heating Rate/High Temperature*

Heating times in the range of 20–500 μs to a chosen high temperature can be achieved by T-jump methods.[2,22] Wenograd[2] quotes heating rates of $2.5 \times 10^7$ K/s for an explosive packed into a hypodermic needle. These rates are undoubtedly optimistically fast because models indicate that the rate of heat transfer to the explosive cannot keep pace with the heat that is believed to be supplied.[23] Heating times of <100 μs to a chosen temperature are important because they simulate conditions that exist during mechanical impact and during combustion. In fact, a frequently used index of the sensitivity of an explosive to mechanical impact is the drop-weight impact test. The impact sensitivity is the height, $H_{50}$, that a weight of given mass must be dropped onto the sample to produce an explosion 50% of the time. The duration of heating during impact is 200–300 μs,[24] and the pressure achieved is 7–15 kbar. In addition to the chemical reactions, $H_{50}$ is affected by a score of other variables including the particle size, hardness of the crystals, the defect number, the defect volume, the crystal size distribution, the atmospheric conditions, and the operator technique. Given the many factors that influence the impact sensitivity, numerous shots are averaged while holding constant as many of the variables as possible. Not surprisingly, considerable scatter in the data occurs.

Robertson and Yoffe[1] concluded that chemical decomposition during impact is very similar to that at less rapid heating rates. This notion was extended by Wenograd[2] who found that the impact sensitivity of a series of diverse explosives roughly correlated with the temperature required to produce an explosion in 250 μs. Thereby, he too concluded that impact sensitivity was linked to thermally induced chemistry. The temperature achieved by several explosives, including TNT, in this time exceeded 1000 °C. This result does not link *thermal stability* with impact sensitivity, because thermal stability is mostly controlled by lower activation energy reaction branches which frequently become deemphasized in favor of higher activation energy branches at higher temperatures.

The drop-weight impact test does not provide chemical details about the thermal processes. To achieve this information, a technique such as T-jump/FTIR spectroscopy[22] can be used. This technique is able to separate and detect some of the dominant reaction branches during rapid heating and to determine the temperature dependence of some of these branches.[22,25]

### *3. High Heating Rate/High Temperature/High Pressure*

The use of a shock wave to heat a material affords a ≤1 μs heating time of localized hot spots to a high temperature. For example, the chemical peak corresponding to 95% decomposition of TNT in a stationary detonation has a duration of 0.4 μs.[26] Pressures for shocked condensed phase materials are in the range of 30–200 kbar. The shock sensitivity of many, but not all, polynitroaromatics for which data are available follows the same trend as the impact sensitivity[27] suggesting that the shock-initiated chemistry is similar to impact-initiated chemistry. However, a considerable body of Russian literature indicates that this is not always the case.[28]

An up-to-date overview of shock and detonation physics of explosives is available elsewhere.[29] In practice shock compression of a solid or liquid can be induced in a number of ways that usually employ a flyer plate. The most common method is to use a standard explosive to transmit a shock wave through a buffer plate to the explosive of interest. Tests known as "wedge" and "gap" are well known to workers in the field. For example, the Navy's small-scale gap test uses a booster explosive in a standard configuration to transmit a high-pressure shock wave through a Plexiglas attenuator to the explosive packed at a particular density compared to the theoretical maximum density. The shock sensitivity is determined by the pressure at which an explosion occurs 50% of the time. For example, $P_{90}$ would be the initiation threshold pressure for an explosive packed at 90% theoretical maximum density. A comparison of various detonation sensitivity tests is given by Urizar *et al.*[30] Electric spark sensitivity has also been compared to shock and impact sensitivity.[31a,b]

For studies of unimolecular reactions in the gas phase at low pressure, a laser pulse[32] or a shock wave created by a burst of gas pressure[33,34] can be used to heat molecules to a high temperature in ≤1 μs. Temperatures in excess of 800 °C can be achieved by shock tube and laser pyrolysis. Lower and higher activation energy processes can be expected to compete effectively with one another under these conditions.

In summary, the reaction temperature and the heating rate play an important role in how the thermal decomposition process of a complex molecule occurs. Some reactions can be expected to be present over a wide range of temperatures while others will not. Consequently, considerable care is needed when comparing the merits of reaction pathways derived from measurements made under diverse conditions.

## B. Experimental Diagnostics for Chemistry of Explosives

Interpretations of the chemistry that is important in an explosive depend on the diagnostic method, because the time resolution, the pressure, the temperature, the sample quantity, and the phase are major variables. The relatively high vapor pressure of many nitroaromatic compounds makes them amenable to study by analytical techniques in the gas phase as well as the condensed phase.

### *1. Dynamic Analysis*

Ideally the course of the reactions could be followed directly in real time. When this condition is achieved for an explosive,[35] the spectral window is narrow and the amount of detailed information is limited. More commonly, simulation of conditions is required to optimize the chemical detail.

Manometry is used extensively in Russia, especially by Maksimov, to determine the rate of gas evolution as a function of temperature for many nitroaromatic compounds. Typically, a 15–20-cm$^3$ glass vessel fitted with a Bourdon-type compensation manometer is immersed in a thermostated bath. Evaporation of the compound is sought so that the decomposition rate can be measured in the gas phase. However, transfer of heat from the glass surface to the nitroaromatic molecule at the temperatures used is primarily by conduction. The molecule must collide with the wall where heterogeneous catalysis can be appreciable. Nevertheless, a large percentage of the rate data for aromatic nitrocompounds has been obtained by this method.

DSC and DTA have been applied extensively to obtain rate data for the condensed-phase decomposition of energetic nitroaromatic compounds. These techniques extract the rate of the processes from the overall heat flow at relatively low temperatures and heating rates. Details of the kinetics are sometimes overshadowed by the fact that energetic materials can generate heat rapidly and the instrument is limited by its ability to detect heat changes instantly. As a result, the rate data are sensitive to the sample size. As with manometry, the global reaction rate is measured. The reactions that are responsible for the decomposition rate must be inferred.

Mass spectrometry is more broadly applicable to the study of thermal decomposition mechanisms of nitroaromatic compounds than it is to many other energetic materials. The foundation of this notion lies in the extensive work of Fields and Meyerson,[36,37] who investigated the mass spectra of numerous nitroaromatic compounds and concluded that the radical cations in the early fragmentation patterns resemble the stoichiometries of products from thermal decomposition routes. This finding cannot be applied broadly to other energetic materials. With nitramines, for example, the species produced by thermal routes and those generated by electron impact must be carefully differentiated.[38]

Electron-impact mass spectrometry yields only the fragments and not their mechanism of formation.[39] Tandom mass spectrometry (MS/MS) used in conjunction with collision-induced dissociation (CID) elucidates the fragmentation pathways of individual ions. The principle is that mass-selected primary ions are fragmented in a reaction cell as a result of collisions with an inert gas. These daughter ions are then analyzed by a second MS, thereby enabling determination of the individual fragmentation pathways of the parent ions.[40]

Electron spin resonance potentially yields mechanistic information, but it is sensitive only to radicals that form and degrade during thermal decomposition in the condensed phase. Very low concentrations ($<10^{-4}$ M) are readily detected. There is no way to prove that the radicals observed are the key species in the decomposition mechanism. Nonradical and ionic pathways are always possible. Assignment of structure and composition of the species is sporting, especially for complicated condensed phase decomposition reactions that produce closely related radicals.

### *2. Post-Reaction Analysis*

Rapid-scan FTIR spectroscopy is a near real-time (~50 ms) analytical technique with a wide spectral window. The gaseous decomposition products at subatmospheric and superatmospheric (~100 atm) can be determined at heating rates up to $2 \times 10^4$ °C/s.[22] Structure/decomposition relationships can be developed[41] and the sequence of product formation outlines the decomposition mechanism.[22,25] The products detected are not the elementary radicals, but the more thermally and kinetically stable species.

Unimolecular decomposition in the gas phase can be induced at high temperature by use of a pulsed laser[32,42] or a shock impulse.[33,34] The quenched products can be analyzed by a variety of techniques, such as by GC–MS.

Essentially the full range of analytical techniques can be applied to analyzing species in a quenched sample that have been generated by heat or mechanical abuse of the material. The caveat is that the most reactive intermediates which are central to the decomposition mechanism at elevated temperature will rearrange and react further upon cooling and during time-delayed analysis. The thermodynamically and kinetically more stable species, therefore, are always detected. These species are only an historical record of the most relevant dynamic processes.

## C. Complexity of Thermal Decomposition in the Condensed Phase

Relatively unperturbed unimolecular decomposition kinetics can be determined only for molecules in the gas phase at low pressure. Materials that are useful as explosives or propellants almost always begin to react in the heterogeneous condensed phase. Thus, while gas-phase studies of individual molecules can be a useful guide to the behavior in other phases, the most important reactions arise when the molecules are in the condensed phase in the presence of like molecules. For instance, by using the oxidation of hydrocarbons as an analogy, the liquid-phase reaction is rarely unimolecular, but the propagation steps can be similar in the liquid and the gas phase.[43]

Qualitative accounts of the decomposition process of bulk TNT and TATB starkly expose that determination of the mechanisms of polynitroaromatic derivatives in the presence of neighboring molecules is an extraordinarily difficult challenge. Robertson[44] described the behavior of TNT when heated to a constant temperature in a closed ampule. TNT melted at 81 °C and partially volatilized, followed by a quiescent period with no gas evolution. Next, gas evolution began accompanied by darkening followed by more rapid gas evolution and then explosion. During the period of darkening, the amount of gas is small (about 1 mol per mole of TNT) and catalysts form.[20] Catalano and

Crawford[45] observed that exothermic decomposition of TATB begins at about 302 °C and found that the reaction stage in the 342–357 °C range necessitated the use of five different rate expressions. These observations are strong reminders that an aggregation of many time-dependent chemical and physical processes exists during the thermal decomposition of a material in the condensed phase. Despite the complications, major temperature segments of the decomposition regime follow Arrhenius behavior, eq 1. $E_a$ is the activation

$$k(T) = Ae^{-E_a/RT} \qquad (1)$$

energy, $A$ is the frequency factor, and $k$ is the reaction rate.

The major perturbations to the elementary decomposition reactions of an isolated polynitrobenzene molecule when the molecule is part of a bulk condensed phase are as follows: (1) bimolecular reactions[46,47] and intermolecular associations[48]; (2) homogeneous and heterogeneous[32,49,50] catalysis[20,34,44,51] by reaction products; and (3) heterogeneous catalysis by the supporting surface and the reactor walls.[7,32,44,48,49,52–56]

Intermolecular association and atom transfer have been proposed by Maksimov[48] to be responsible for the fact that the rate of decomposition of TNT in the melt phase expressed as a first-order rate constant is about 10 times faster than in the gas phase or in solution. On the other hand, most energetic molecules, such as nitrate esters, hexahydro-1,3,5-trinitro-*s*-triazine (RDX), and octahydro-1,3,5,7-tetranitrotetraazacine (HMX) react more slowly in the condensed phase than in the gas phase.[48] In fact, the specific rate constants for many condensed-phase decomposition reactions of polynitroaromatics are $10^5$–$10^{10}$ $s^{-1}$, which is below the limit of $10^{12}$ $s^{-1}$ for many unimolecular reactions and is suggestive of bimolecular processes.[48]

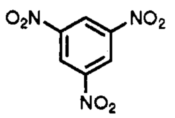
An important factor contributing to the faster rate of condensed-phase reactions compared to the gas phase is catalysis by the reaction products. For this reason virtually every kinetic study of decomposition of polynitroaromatic explosives in the condensed phase, since an early report,[57] has found that an autocatalytic expression is required to fit the rate data. Of course, very small amounts of catalyst can markedly influence the rate of most reactions. In fact, Maksimov[58] proposed that impurities in the original sample sharply change the rate of decomposition of nitroaromatic compounds. Irrespective of the impurities, many compounds,[20,44,51,59,60] including essentially any source of $H^\bullet$ or other radicals, accelerate the rate of decomposition of TNT.[51] TNT and most of its decomposition products produce radicals at the $10^{-4}$ M level[61] when heated below 300 °C. Several specific decomposition products of TNT have been tested and are found to catalyze decomposition of TNT. These include 2,4,6-trinitrobenzaldehyde,[20] 2,4-dinitroanthranil (2,4-DNAn),[51,59] and ill-defined explosive "coke" from long-term thermal degradation,[20] and elemental carbon.[62] The role of catalysis by low levels of decomposition products is not readily separable from the role of intermolecular associations[48] mentioned above. Therefore, catalysis rather than intermolecular association of TNT molecules may be reponsible for the faster rate of decomposition of TNT in the condensed phase compared to the gas phase.

The influence of catalysis by the walls of the reactor and the supporting surface of the sample has been mentioned by many authors as a potential factor in the reaction rate,[7,32,44,48,49,52–54,63] but has been investigated systematically in only a few studies. For example, Maksimov[53] found that increasing the surface area of the glass reaction vessel (type of glass not given) with the aid of capillaries greatly accelerated the initial rate of decomposition of trinitrobenzene derivatives in the vapor phase. Since the wall and bulk-phase decomposition mechanisms are thought to be the same,[46,53,63] it is difficult to separate the role of catalysis by the decomposition products from the role of surface catalysis.

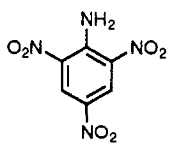
One of the more helpful empirical insights for sorting out thermal decomposition schemes of trinitrobenzene derivatives in the condensed phase is the observation that initial fragmentation patterns in the EI mass spectrum seem to parallel thermal decomposition schemes in the gas phase.[36,37,64,65] Moreover, it is helpful that the early thermal decomposition products found in the gas phase closely resemble the stable intermediates formed by heating the condensed phase. While the elementary steps leading to these molecules are undoubtedly altered somewhat by the phase, the similarity of the stable species in the gas phase and the stable intermediates in the condensed phase supports a role for them in the decomposition sequence, at least under certain conditions. However, because of the catalysis by the decomposition products and the intermolecular interactions mentioned above, there is no reason to expect that the reaction details of a nitrobenzene derivative in the gas phase or in dilute solution will be the same as in the bulk condensed phase.

### D. Uncertainty about Determining Molecular Control over Explosive Behavior

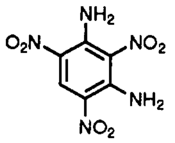
It was noted in section I that there are strong reasons to believe that thermochemistry is in some way connected to impact and shock initiation of explosives.[1–12,27,66] The desire to understand the controlling molecular mechanisms of impact and shock sensitivity of an explosive has led to many published correlations of explosive data with molecular properties. The most extensive of these compilations for nitroaromatic compounds are by Kamlet and Adolph,[24] Zeman,[5–8,54] and Storm *et al.*[27] A number of other correlations of molecular and crystal parameters with explosives behavior have been given for the limited, but attractively related, set of the four compounds TNB, MATB, DATB, and TATB. However, this series is also an excellent



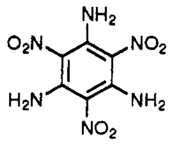
TNB



MATB



DATB



TATB

**Table I. Sensitivity and Performance Parameters**

| compd | $H_{50}$, cm | $P_{90}$, kbar[c] | $P_{C\text{-}J}$, GPa[d] | $\Delta H^{e}_{ex}$, kJ g$^{-1}$ |
|---|---|---|---|---|
| TNB | 100[a] | 15 | 22.9 | 4.734 |
| MATB | 177[a] | 28 | 24.7 | 4.263 |
| DATB | 320[a] | 46 | 26.7 | 4.138 |
| TATB | 490[b] | 70 | 29.3 | 3.990 |

[a] Reference 24. [b] Estimated, but frequently used, see refs 27 and 72. [c] References 5, 27, and 67. [d] Reference 7. [e] Reference 6.

**Table II. Compositional and Crystal Parameters**

| compd | MW, g mol$^{-1}$ | $\rho$, g cm$^{-3}$ | $\rho N^{e}$, g cm$^{-3}$ | $\Delta H_f°$, cal g$^{-1}$ | melting point, K | $OB_{100}$ |
|---|---|---|---|---|---|---|
| TNB | 213 | 1.688[a] | 0.653 | −41.8 | 396 | −1.46 |
| MATB | 228 | 1.760[b] | 0.646 | −78 | 461 | 1.75 |
| DATB | 243 | 1.837[c] | 0.628 | −122.6 | 559 | −2.06 |
| TATB | 254 | 1.938[d] | 0.623 | −143 | 623[f] | −2.33 |

[a] Reference 68. [b] Reference 69. [c] Reference 70. [d] Reference 71. [e] Reference 72. [f] Not uniformly agreed upon (see text).

illustration of the pitfalls of correlating of molecular variables with explosive properties in an attempt to find the controlling mechanism. For TNB, MATB, DATB, and TATB these variables are catagorized according to whether the basis is predominantly the explosive characteristics (Table I), the composition and crystal properties (Table II), or the molecular and electronic structure (Table III). Most of the entries are self-explanatory, but a few require brief description. The impact sensitivity, $H_{50}$, the shock initiation threshold pressure, $P_{90}$, and the Chapman–Jouguet pressure, $P_{C\text{-}J}$, were defined in sections I and II.A. $\Delta H_{ex}$ is the heat of explosion. In Table II, $\rho N$ is the density of $-NO_2$ groups in the crystal lattice defined by eq 2,[72] where $Z$ is the number of molecules in the unit cell, $M$ is the $NO_2$ molecular mass per molecule, and $V$ is the unit cell volume. The oxidant balance, $OB_{100}$, is defined

$$\rho N = \frac{ZM}{V} \tag{2}$$

according to eq 3 as the number of equivalents of oxygen in 100 g of a CHNO explosive required to convert all of the H to $H_2O$ and C to CO. $N$ is the number of atoms

$$OB_{100} = \frac{100\,(2N_O - N_H - 2N_C - 2N_{COO})}{MW} \tag{3}$$

of each element in the formula. The melting point is partly a reflection of the intermolecular cohesive forces. In Table III, the electrostatic potential calculated at the midpoint of the $C-NO_2$ bond, $V_{mid}$, determined by a Mulliken orbital population analysis at the level of CINDO,[73] and *ab initio* SCF-MO with STO-3G[74] or STO-5G[75] basis sets. The number of aromatic $\pi$ electrons was calculated at the STO-3G level.[67] The shake-up promotion energy separation, ΔSPE, of N(1s) of the $-NO_2$ groups was obtained by X-ray photoelectron spectroscopy.[76] The average bond distances were obtained from the crystal structures.[68-71]

Perusal of the columns of Tables I–III and of the tables relative to one another reveals that a trend exists in all columns. To emphasize the similarity, the correlation coefficient, $R^2$, and the confidence level of statistical significance according to the $t$ test[77], eq 4, are given in Table IV for all columns plotted versus the

$$t = R\left(\frac{n-2}{1-R^2}\right)^{1/2} \tag{4}$$

impact sensitivity, $H_{50}$. To exceed 95% confidence, the value of $t$ for four data points ($n$) must exceed 3.18. In all cases except one, this confidence level is achieved. In fact, 12 data sets exceed 99% confidence ($t > 5.84$). The only case that fails 95% exceeds 90% confidence ($t > 2.35$). Furthermore, two sets of data that are linearly related to a third are linearly related to each other. Therefore, among the 18 sets of data in Tables I–III, there are 153 positive correlations. A few of course are dependent or, at least, interconnected. The density and C–J pressure are related through the detonation velocity, $D$, by eq 5. The molecular weight enters into

$$P_{C\text{-}J} \simeq 0.25\rho D^2 \tag{5}$$

$OB_{100}$ by eq 3. The increase in the average C–C and N–O distances is paralleled by the decrease in the average $C-NO_2$ distance as $-NH_2$ groups are added. In some cases the correlations are folly even though $R^2$ is high. For example, melting point vs shake-up promotion energy separation, heat of formation vs density, molecular weight vs the $C-NO_2$ midpoint electrostatic charge are among the more chemically ridiculous correlations.

On the other hand, several of the correlations of the columns in Tables I–III have been proposed to identify crystal and molecular factors that influence the impact and shock sensitivity of TNB, MATB, DATB, and TATB. The correlation of $H_{50}$ in Table I with the shake-up promotion energy separation[76,78] (Table III) was proposed as evidence of the importance of excited states in determining the impact sensitivity.[78] Correlation of $H_{50}$ with $V_{mid}$ in Table III has been suggested to show that the $C-NO_2$ bond strength and homolysis play a role[74,75] or are rate controlling[73] in the impact and shock sensitivity of the TNB, MATB, DATB, TATB series. Table IV reveals that the average $C-NO_2$ bond distance correlates as well or better with $H_{50}$ as does $V_{mid}$. In fact, all of the trends in Table III principally result from systematic ground-state electronic and structural trends along this series. That is, the C–C, $C-NO_2$, and N–O bond distances are no more or less "controlling" of the sensitivity than any other factor at this level of analysis. Systematic differences in the bond distances figure importantly into the computed electrostatic potentials and measured relative orbital energies.

Other correlations of data in Table II with $H_{50}$ have been made. Odiot[72] noted that the density of $-NO_2$ groups in the crystal correlated with $H_{50}$. Kamlet and Adolph[24] correlated $OB_{100}$ with the log $H_{50}$ for TNB, MATB, DATB, and TATB and other compounds. The trends implied that the oxidizing potential of the molecule may be important. Table III reveals that for this series of compounds, $H_{50}$ correlates as well with $OB_{100}$ as does log $H_{50}$. Storm *et al.*[27] noted that within Table III, $H_{50}$ and $P_{90}$ correlate well. Rogers *et al.*[67] proposed that the increasing amount of intermolecular hydrogen bonding as $-NH_2$ groups are added is responsible for the decrease in shock sensitivity. As intermolecular hydrogen bonds increase in number, they are proposed to absorb energy from the shock front and prevent it from being localized in the molecule.[67] Although difficult to quantify with the data available,

**Table III. Molecular and Electronic Parameters**

| compd | $\bar{V}_{mid}$, au STO-5G[a] | $\bar{V}_{mid}$, au STO-3G[b] | $\bar{V}_{mid}$, au CINDO[c] | no. $\pi e^-$ | ΔSPE,[e] eV | $d$, Å C–$NO_2$ | $d$, Å N–O | $d$, Å C–C |
|---|---|---|---|---|---|---|---|---|
| TNB | 0.208 | 0.197 | 0.012 | 5.96[d] | 0 | 1.482[f] | 1.199[f] | 1.380[f] |
| MATB | 0.174 | 0.168 | –0.018 | 6.16 | 0.8 | 1.469[g] | 1.219[g] | 1.393[g] |
| DATB | 0.146 | 0.130 | –0.048 | 6.36 | 2.1 | 1.454[h] | 1.233[h] | 1.411[h] |
| TATB | 0.103 | 0.102 | –0.063 | 6.54 | 2.7 | 1.419[i] | 1.243[i] | 1.442[i] |

[a] Reference 75. [b] Reference 74. [c] Reference 73. [d] Reference 67. [e] Reference 76. [f] Reference 68. [g] Reference 69. [h] Reference 70. [i] Reference 71.

**Table IV. The Coefficients of Correlation and the Confidence Level Based on the "*t*-test" for Plots of all Entries in Tables I–III versus the Impact Sensitivity Index, $H_{50}$**

| parameter | correlation coefficients $R^2$ | $t$ (eq 4)[a] |
|---|---|---|
| $P_{90}$ | 0.998 | 31.6 |
| $P_{C-J}$ | 0.992 | 15.75 |
| $\Delta H_{ex}$ | 0.773 | 2.61 |
| MW | 0.952 | 6.30 |
| $\rho$ | 0.991 | 14.83 |
| $\rho N$ | 0.927 | 5.04 |
| $\Delta H_f°$ | 0.931 | 5.20 |
| mp | 0.972 | 8.33 |
| $OB_{100}$ | 0.971 | 8.18 |
| $V_{mid}$, STO-5G | 0.982 | 10.45 |
| $V_{mid}$, STO-3G | 0.972 | 8.49 |
| $V_{mid}$, CINDO | 0.919 | 4.76 |
| ΔSPE | 0.950 | 6.17 |
| no. $\pi$ $e^-$ | 0.968 | 7.78 |
| $d_{C-NO_2}$ | 0.981 | 10.17 |
| $d_{N-O}$ | 0.955 | 4.55 |
| $d_{C-C}$ | 0.994 | 18.2 |

[a] Significant at confidence level 90% ≥ 2.35; 95% ≥ 3.18; 99% ≥ 5.84.

a qualitative indication of the trend in intermolecular association in the series is the melting point, and, possibly, the density. Both increase as $-NH_2$ groups are added to the ring and the shock sensitivity, $P_{90}$, decreases.

An inescapable conclusion of Tables I–IV is that single column correlations of the molecular, lattice, and explosive properties for TNB, MATB, DATB, and TATB are not especially helpful for identifying the primary chemical mechanisms of shock and impact sensitivity. Correlations within a given table are the soundest. It is especially risky to pick a column of one table and correlate it with a column in another table. For example, any column of Table III is as justifiable as any other to correlate with $H_{50}$ in Table I. As a result, previous conclusions about molecular features that control shock and impact sensitivity in this series of compounds are contradictory: excited electronic states[78] vs C–$NO_2$ midpoint electrostatic potential[73–75] vs intermolecular hydrogen bonding[67] vs oxidant balance.[24] With 153 positive correlations among the data, single correlations are unlikely to provide the true controlling factors. Perhaps all of these factors (or none of them) contribute to the sensitivity to some degree.

Given the enormous barriers to obtaining meaningful data on the condensed-phase decomposition mechanisms of nitroaromatic explosives (i.e. temperature effects, pressure effects, shortcomings of diagnostics, catalysis, bimolecular processes, rapid heat generation, parallel properties, etc.), it is not surprising that contradictory data and interpretations are common. In the following sections the merits of kinetics and mechanistic models of thermal decomposition are evaluated.

## *III. Global Kinetics of Thermal Decomposition*

Most knowledge about the thermal decomposition kinetics of explosives is obtained from rate measurements at relatively low temperature (<400 °C). Kinetic data for TNT are cited in this section along with some discussion of the merits of measurement methods. These kinetic data are used in later sections to aid in determining the reaction mechanisms.

As mentioned in section II.C, the decomposition process of bulk TNT involves a solid-to-liquid phase change. Reactions in the liquid phase lead to a small amount of gas and nonvolatile intermediate products, followed by other reactions that produce a large quantity of lower molecular weight gases. It is widely agreed[44,79,80] that the overall process in the liquid phase is modeled by a first-order rate expression (eq 6), where $\alpha$ is the amount of sample decomposed and $t$ is time. Autocatalysis and self-heating complicate the interpretation of the kinetics. Therefore, attempts to measure $k(T)$ are usually made under adiabatic or isothermal conditions whose relationship to $k(T)$ for a first-order process is given by the heat balance eq 7.[9] $\lambda$ is the thermal diffusivity; $C$ is the specific heat; and $Q$ is the heat of reaction. The first term of eq 7 accounts for heat loss to the surroundings. The second term is the heat accumulated by the explosive. The sum of these two terms equals the heat generated by the thermal decomposition. Equation 7 cannot be solved under nonisothermal, nonadiabatic conditions. However, under adiabatic conditions ($\lambda\nabla^2T = 0$), such as time-to-explosion or time-to-exotherm (TTX) experiments,[11,44,81a] the apparent activation energy can be calculated from eq 8, where $t_e$ is the time-to-exotherm at temperature $T$. Gray[81b] described such activation energies as "molehills of knowledge". This assessment is reasonable in the sense that a major effort needs to be expended to separate the rate of heat transfer to the sensor from the rate of heat release by the chemical reactions.[23] Under isothermal conditions ($dT/dt = 0$ in eq 7), such as is achieved by evolved gas and DSC methods, Arrhenius constants are obtained from eq 1.

$$\ln(1 - \alpha) = k(T)\,t \qquad (6)$$

$$-\lambda\nabla^2T + \rho C(dT/dt) = \rho QA(1 - \alpha)e^{-E_a/RT} \qquad (7)$$

$$\ln t_e = \frac{E_a}{RT} + \gamma \qquad (8)$$

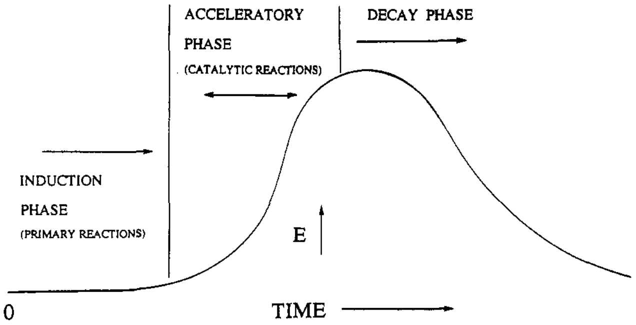


**Figure 1.** The energy release trace for slow decomposition of a nitroaromatic at a relatively low temperature.

Figure 1, which is an idealized representation of the DSC thermogram of TNT, can be subdivided into three regions.[82] On the basis of eq 7, the induction period represents the length of time that the sample is thermally quiescent after heating to a set temperature. Activation energy determined during this period may have the best chance of being related to the structure of the parent molecule, since it reflects the earliest reaction events. The acceleratory stage is the time during which catalysis and self-heating dominate the rate of decomposition. The decay phase is the time when mostly later stage decomposition products react. In reality, the kinetics of decomposition of a bulk sample of an explosive are also sensitive to the mass and geometry of the sample. One reason is that the rate of heat transfer into and out of the sample cannot keep pace with the chemical reaction. Hence, the heat changes detected are partly a measure of the reaction rate and partly a measure of the heat transfer rate.[23] Mass transport may also occur at a different rate than the reaction rate. Under these circumstances, agreement among measured rate parameters obtained by different techniques is unlikely. Moreover, association of the rate of the process during any of the phases in Figure 1 with a specific reaction is necessarily simplistic.

The Arrhenius parameters for TNT are compiled in Table V, and fall into three groups according to the stages shown in Figure 1. These data apply below 400 °C and are not necessarily representative of the chemistry at high temperature that is initiated by shock and impact. Considerations of mechanisms at higher temperature are discussed in more detail in section IV. Most publications in the past 15 years mention the stage of Figure 1 that is believed to be studied. Older literature rarely discusses the reaction stage. If not noted, the data were grouped according to the $E_a$ value. The Arrhenius constants of the induction phase tend to be higher than the other stages perhaps because they are most closely related to a bond-breaking step. Maksimov[84] attributes his data during induction to unimolecular processes. In the acceleratory stage, the Arrhenius constants are smaller perhaps because of catalysis by the decomposition products. Maksimov[84] attributes his rate data in this stage to bimolecular processes. The measurement by Urbanskii and Rychter[85] gives the lowest $E_a$ value of all probably because the temperature exceeds the boiling point of TNT (345 °C).[44] Wenograd's low value of $E_a$ was determined at high temperature and high heating rate on a semiconfined sample.[2] It is nearly impossible to achieve sufficiently rapid heat transfer and temperature sensing under Wenograd's conditions to obtain an accurate value of $E_a$.[23] In fact, global activation energies determined at high heating rates and high temperature frequently are smaller than those at lower heating rate and lower temperature,[88,89] probably because the rate of heat transfer is important. The value of Brill and James[87] was obtained at 2000 °C/s under 30 atm Ar to suppress evaporation and does not suffer this problem. The one measurement of Arrhenius parameters that is clearly stated to be of the decay phase[82] is similar to, but slightly less than, the acceleratory phase.

**Table V. Arrhenius Parameters for Thermal Decomposition of TNT (Data are Arranged Qualitatively According to the Stage of the Process Measured)**

| $T$, °C | $E_a$, kcal/mol | A, $s^{-1}$ | method[a] | ref |
|---|---|---|---|---|
| | Induction Phase | | | |
| 203–283 | 40.9 ± 1.6 | | ESR | 80 |
| 298–490 | 41.4 | $10^{13.2}$ | TTX | 81 |
| 237.5–276.5 | 43.4 ± 0.8 | $10^{12.19\pm0.32}$ | EG | 79 |
| 140–180 | 46 ± 3.7 | | EG | 83 |
| 220–260[b] | 46.5 | $10^{12.9}$ | EG | 84 |
| 245–269 | 46.5 ± 1.5 | | IDSC | 82 |
| 240–255 | 50.7 ± 2.4 | | DTA | 55 |
| | Acceleratory Phase | | | |
| 390–450 | 14 | | TTX | 85 |
| 500–720 | 18 | $10^{6.6}$ | TTX | 2 |
| ~300 | 27 | | TTX | 57 |
| 203–283 | 30.2 ± 0.6 | | ESR | 80 |
| 275–310 | 32.0 ± 2.5 | | TTX | 44 |
| 390–407 | 34 | | TTX | 87 |
| 275–310 | 34.4 ± 2.5 | $10^{11.4}$ | EG | 44 |
| 280–320 | 34.5 | $10^{8.45}$ | EG | 53 |
| 190–270 | 34.6 | $10^{9.3}$ | EG | 86 |
| 220–260[b] | 35.6 | $10^{9}$ | EG | 84 |
| | Decay Phase | | | |
| 245–269 | 29.4 ± 1.4 | $10^{9.9}$ | IDSC | 82 |

[a] EG = manometric measurement of evolved gas; TTX = time-of-explosion (exotherm); IDSC = isothermal differential scanning calorimetry; DTA = differential thermal analysis. [b] However, rate data in figures of ref 84 given at 280–330 °C.

The methods of measurement of the Arrhenius data in Table V reflect all of the complications of kinetics determinations of thermal decomposition of bulk-phase explosives. Manometric measurement of the rate of gas evolution from nitrobenzene explosives has been used extensively in Russia especially by Maksimov and co-workers. They described manometry as measuring decomposition in the vapor phase, but noted that substituted nitrobenzene compounds occasionally form a brown residue on the reactor wall.[53] As discussed in section II.C, catalysis by this residue contributes to the reaction rate. Use of the manometric method for rate measurements has been criticized[20,80,81a,82] because the amount of gas generated by trinitrobenzene derivatives depends on the amount of nonvolatile residue that forms and the mechanism of the reaction. Moreover, many substituted trinitrobenzene explosives have significant vapor pressure at elevated temperature.[90] The vapor-pressure equation for TNT is given by eq 9.[44,91]

$$\log P(\text{mmHg}) = 9.11 - 3850/T \qquad (9)$$

Fortunately, knowledge of the vapor pressure enables the sample size to be chosen to ensure that all of the decomposition occurs in the vapor phase. Table V reveals that the activation energies from manometry are similar to those obtained by other techniques.

Consequently, criticisms of manometry, while probably valid, do not disqualify the data and do not strengthen confidence in any other method of kinetics measurement.

Various methods of measuring the time-to-exotherm (explosion) involve sensing the time of violent release of heat or explosion. Equation 8 is used to determine the apparent activation energy. Numerous studies employ this method and a characteristic of most data is curvature[2,80,81a,92-95] in the plot of ln $t_e$ vs $1/T$. The inability to control the heat transfer rate and to know the true temperature makes the value of $E_a$ sensitive to the assumed temperature. Perhaps the best-controlled method for measuring the length of the induction period is isothermal DSC.

Measurement of the rate of growth of the ESR signal of a paramagnetic species has been used to determine the rate of the induction and acceleratory phase of TNT decomposition.[80] Following the concentration of a particular species in this way is more directly related to a reaction than the global rate measurements by EG or DSC, but assumes that the reaction involving the paramagnetic species occurs at the same rate as the overall decomposition process. This is not the case for TNT.[80]

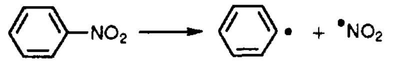
In sum, there is no completely unambiguous method to measure the rate of decomposition of an energetic material in the bulk state. Fortunately, rough agreement exists among measurements on TNT made by several different methods. Rate data exist for decomposition of other nitroaromatic compounds[5,6,8,47,50,52,53-56,84,86,96-106] some of which are used later in this article.

## *IV. Early Thermal Decomposition Reactions*

Several of the thermal decomposition reactions of polynitroaromatic compounds involve simple bond scission or rearrangements of the substituents on the ring. These are among the first few reactions and thereby initiate all subsequent steps in the complex decomposition scheme. This section evaluates these reactions beginning with the nitro group and concluding with reactions of other substituents on the benzene ring, particularly those *ortho* to the $-NO_2$ group. A notable feature of these reactions is the fact that the aromatic ring remains intact. Destruction of the aromatic ring is a later stage process described in section VI.

### A. C–NO$_2$ Homolysis

Simple homolysis of the C–NO$_2$ bond to form an NO$_2$ radical and an aromatic radical by eqs 10 is a logical reaction on the basis of the importance of the analogous reaction in nitroaliphatics, nitramines ($R_2NNO_2$), and nitrate esters ($RONO_2$).[107] For these latter compounds



(10)

the X–NO$_2$ bond is usually the weakest bond in the molecule. Two observations suggest, however, that simple extension of this analogy to nitroaromatic compounds requires qualification. First, the bond dissociation energy (BDE) of nitrobenzene derivatives is known to be about 71 kcal/mol[32] and is altered by only 1–4 kcal/mol by adding an $\alpha$-$CH_3$ group,[32] an additional $-NO_2$ group,[32,52] or Cl, Br, I, NH$_2$, and OH[52] to the ring. The $C_6H_5$–$NO_2$ BDE is significantly larger than that of an aliphatic carbon-bound $-NO_2$ group (about 60 kcal/mol), a nitramine (about 50 kcal/mol), and a nitrate ester (about 40 kcal/mol).[108] Second, although $NO_2$(g) has been reported from decomposition of nitrobenzene at 275 °C[109] and from pyrolyzed 1,3-dinitrobenzene,[110] 1,4-dinitrobenzene,[110] and 1,3,5-trinitrobenzene[111] by MS, $NO_2$(g) is rarely observed from decomposition of substituted nitrobenzene compounds in the bulk state. This behavior sharply contrasts with the behavior of nitroaliphatics, nitramines, and nitrate esters, where $NO_2$(g) is a readily detected product.[107] Both of these observations suggest that nitroaromatic compounds may have alternate decomposition channels whose activation energies lie below that of C–NO$_2$ homolysis, especially when other substituents are present on the ring.

Table VI. Arrhenius Data for C–NO$_2$ Homolysis of Mono-, Di-, and Trinitrobenzene Compounds

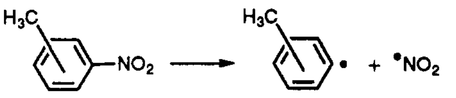
| compound | $T$, °C | $E_a$, kcal/mol | $A$, s$^{-1}$ | ref |
|---|---|---|---|---|
| $C_6H_5NO_2$ | 410–480 | 69.7 ± 1.4 | $10^{17.3\pm0.3}$ | 52 |
| | 455–530 | 67.3 ± 4.7 | | 112 |
| | 797–907 | 65.7 | $10^{15.3}$ | 33 |
| | 827–977 | 68.2 ± 1.7 | $10^{15.5\pm0.5}$ | 32 |
| 1,3-$(NO_2)_2C_2H_4$ | 420–480 | 68 ± 3 | $10^{16.8\pm0.5}$ | 52 |
| | 827–977 | 70 ± 2.1 | $10^{14.5\pm0.5}$ | 32 |
| 1,4-$(NO_2)_2C_6H_4$ | 420–470 | 68.6 ± 2.5 | $10^{17.1\pm0.5}$ | 52 |
| 1,3,5-$(NO_2)_3C_6H_3$ | 380–470 | 67.3 ± 0.8 | $10^{17.2\pm0.2}$ | 52 |

Table VII. Arrhenius Data for C–NO$_2$ Homolysis of Mononitrotoluene (NT) and Dinitrotoluene (DNT) Derivatives

| compd | $T$, °C | $E_a$, kcal/mol | $A$, s$^{-1}$ | ref |
|---|---|---|---|---|
| 2-NT | 797–907 | 61.47 | $10^{14.81}$ | 33 |
| | 827–977 | 67.0 ± 2.2 | $10^{16.4\pm0.6}$ | 32 |
| 3-NT | 300–350 | 65 | $10^{17.88}$ | 96 |
| | 400–470 | 68 | $10^{16.9}$ | 52 |
| 4-NT | 300–350 | 61.5 | $10^{16.73}$ | 96 |
| | 400–470 | 65.9 | $10^{16.7}$ | 52 |
| | 797–907 | 64.29 | $10^{14.89}$ | 33 |
| | 827–977 | 68.2 ± 2.0 | $10^{14.9\pm0.5}$ | 32 |
| 2,4-DNT | 827–977 | 67.4 ± 1.7 | $10^{15.3\pm0.4}$ | 32 |

Table VI lists Arrhenius parameters for C–NO$_2$ homolysis from unsubstituted nitroaromatic compounds (eq 10) in the gas phase. The process is first order.[52] Earlier literature values of $E_a$ for thermal decomposition of nitrobenzene of 51–52 kcal/mol[113,114] are either in error or do not refer to simple bond homolysis. The values of $E_a$ in Table VI are very similar to the BDE of $C_6H_5$–$NO_2$, which is good evidence that the activation energy corresponds to C–NO$_2$ homolysis.[115] As noted above, pyrolysis of 1,3- and 1,4-dinitrobenzene[110] and 1,3,5-trinitrobenzene[111] in the gas phase produces ions corresponding to the successive loss of NO$_2$. The rate constants for decomposition of these three compounds in the gas phase at 330 °C are in the ratio 1:20:34.[53] The primary loss of NO$_2$ from these molecules leaves the aromatic fragment with the vibrational and electronic internal energy for further reaction.[111]

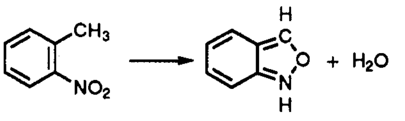
C–NO$_2$ homolysis by eq 11 is a dominant decomposition channel of 3- and 4-nitrotoluene, and also occurs for 2-nitrotoluene.[32-34,36,52,96,116a] Table VII lists the Arrhenius data for eq 11. While only rough agreement exists among these data, the $E_a$ values are similar to



(11)

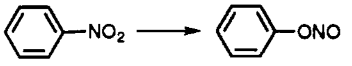
the BDE of C–NO$_2$. The relatively large $A$ factor is characteristic of unimolecular bond scission and produces a positive entropy of activation. Using Maksimov's data,[96] $\Delta S^{\ddagger}$ is about 20 cal/deg for 3-NT and 14.5 cal/deg for 4-NT. C–NO$_2$ homolysis has been suggested to be the initial reaction of *para*-substituted nitrobenzene compounds on the basis of DSC and accelerating rate calorimeter data where the temperature at the onset of decomposition roughly correlates with the electron-withdrawing and -donating effect of the substituent.[116b]

In the gas phase, C–NO$_2$ homolysis in 2-NT competes with other reactions. These reactions have been addressed by Tsang and co-workers[33,34] and McMillen, Golden, and co-workers.[32,42] Equation 12, the formation of anthranil, was found to be an important reaction channel in laser-assisted homogeneous pyrolysis[32] and in shock tube pyrolysis.[33,34] This reaction has been



(12)

known throughout the 20th century and is discussed in further detail in section IV.D.1. The rate constant of eq 12 in the gas phase is $k = (1.2 \times 10^{10}) \exp(-51520/RT)$ s$^{-1}$. Tsang *et al.*[34] also found a third reaction attributed to isomerization of the –NO$_2$ group, which is represented by



(13)

and with $k$ estimated to be $10^{13} \exp(-55980/RT)$ s$^{-1}$. However, a discrepancy exists concerning the relative importance of eqs 11 and 12. Equation 12 was found to dominate in the studies of Tsang *et al.*[33,34] while eq 11 dominated in the studies of McMillen, Golden, and co-workers.[32,42] In both the laser pulse and the shock tube, the temperature of the reactant is stepped in several microseconds to the 800–1000 °C range. Ideally, the T-jump has a square wave form, but in reality the shock front can be nonhomogeneous and the laser beam does not have a uniform energy cross section. The different conclusions about the relative importance of reaction channels of eqs 11 and 12 were proposed[33,34] to originate from uncertainty about the reaction temperature. Both studies[32,34] use the "comparative rate" technique employing an internal standard to measure an effective temperature, which is usually not extracted. A 100 °C higher temperature in the laser pyrolysis studies could account for the different results.

Figure 2 shows Arrhenius plots of eqs 11–13 using the rate constants of Tsang *et al.*[33,34] for eqs 12 and 13 and the 2-NT data for eq 11. Of the three reactions in the gas phase, eq 12 has the fastest rate up to 950 °C. At this temperature eq 11 becomes the fastest reaction. A similar analysis of the relative rates of decomposition channels can be made of 1,3,5-trinitrobenzene versus 2,4,6-trinitroaniline. C–NO$_2$ homolysis of TNB equivalent to eq 11 has a rate constant[52] of $k = 10^{17.2} \exp(-67300/RT)$ s$^{-1}$. 2,4,6-Trinitroaniline is known to decompose by two branches shown in eq 14 to the furazan and furoxan derivatives. These cyclized prod-

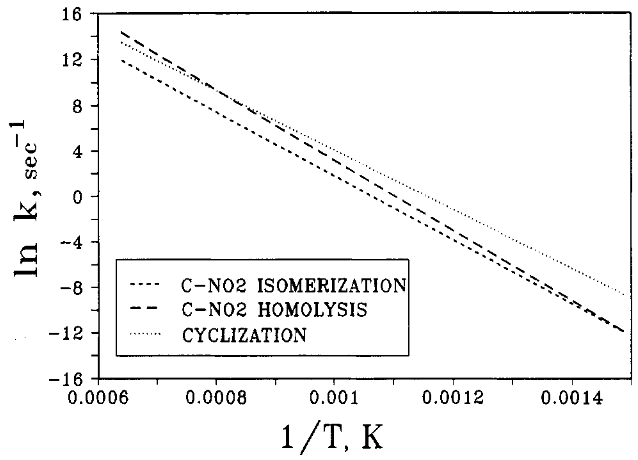


**Figure 2.** Arrhenius plots of the rates of decomposition of 2-nitrotoluene by the three main channels.

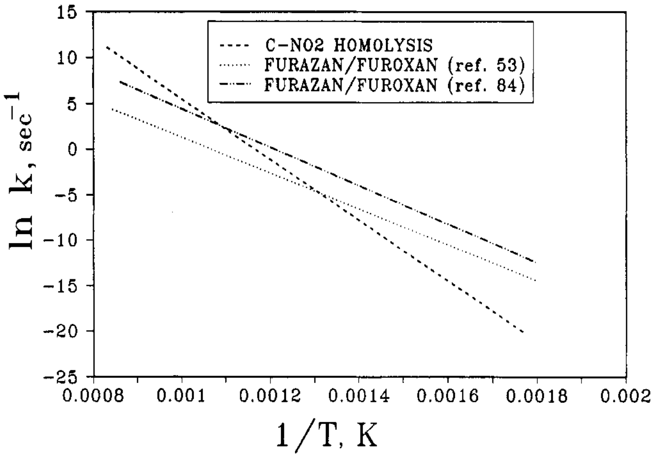
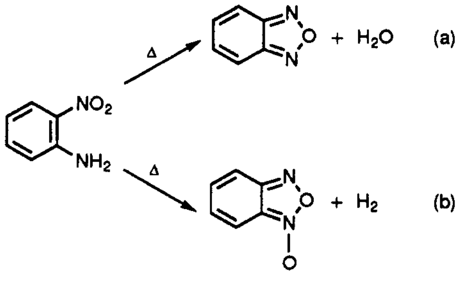


**Figure 3.** Arrhenius plots of the rates of decomposition of MATB in the gas phase by C–NO$_2$ homolysis and furazan/furoxan formation.



(14)

ucts are equivalent to eq 12 for nitrotoluene. Two gas-phase rate constant measurements are available[53,84] for eq 14 giving $k = 10^{8.8} \exp(-38500/RT)$ s$^{-1}$ and $k = 10^{11} \exp(-41800/RT)$ s$^{-1}$. Figure 3 shows a plot of these three rate constants. The cyclization reactions of eq 14 are the favored process below 475 or 625 °C depending on which rate constant is chosen for 2,4,6-trinitroaniline. C–NO$_2$ homolysis is the favored process above these temperatures.

The conclusion reached from the appearance of Figures 2 and 3 is that C–NO$_2$ homolysis is the favored decomposition channel of nitroaromatic compounds in the gas phase when the temperature is high. The cyclization decomposition channels dominate at lower temperature.

All of the discussion above pertains to the gas-phase pyrolysis mechanism. Reactions in the condensed phase can be strongly affected by near-neighbor interactions. For example, C–$NO_2$ homolysis in the condensed phase may be assisted by intermolecular $H^{\bullet}$ atom transfer[48] to produce HONO rather than $NO_2^{\bullet}$. In this case, a concerted process involving both C–H and C–$NO_2$ homolysis might determine the rate constant. Moreover, during shock and impact initiation, the temperatures reached are relatively high. For instance, Wenograd[2] estimated that TNT and TNB reach 1000–1100 °C during impact initiation. Consequently, C–$NO_2$ homolysis is likely to be competitive with other decomposition channels under shock and impact initiation. In fact, a number of studies conclude that shock and impact initiation of nitrobenzene derivatives correlate with attributes of the C–$NO_2$ bond. Owens[73] and Politzer *et al.*[74,75] correlated impact sensitivity with the electrostatic potential at the midpoint of the C–$NO_2$ bond. Delpuech and Cherville[117–119] correlated impact sensitivity with an index derived from the polarity of the C–$NO_2$ bond in the ground and excited states of nitroaromatic compounds.

Assertions that the rate of C–$NO_2$ homolysis is fundamentally important in the impact and shock sensitivity of nitroaromatic compounds[73,75] directly contradict conclusions drawn from other studies. In particular, Kamlet and Adolph[24] were able to separate the impact sensitivities of nitroaromatic compounds into two categories—those having and those lacking $\alpha$-CH bonds *ortho* to the –$NO_2$ group on the ring. These results are discussed in greater detail in section IV.D.1. They imply that reactions of the $\alpha$-CH bond as in eq 12 are important during the impact initiation process. In fact, Dacons *et al*[20] proposed that bimolecular oxidative insertion of O into the CH bond was the initial and rate-determining step. Bulusu and Autera[66] observed a small positive deuterium isotope in the shock sensitivity and detonation velocity when TNT and TNT-$\alpha$-$d_3$ were compared. Because a primary isotope effect is also observed during slow decomposition of TNT,[51] they concluded that the RDS of slow decomposition, shock initiation, and detonation is the same and involves C–H bond rupture. The small size of the isotope effect implies, however, that significant dilution has taken place during shock initiation and detonation.

The direct conflict concerning whether C–$NO_2$ homolysis or $\alpha$-CH bond scission is rate controlling in nitroaromatic compounds may simply stem from the temperature conditions of the experiment. As shown in Figure 2, the rates of C–$NO_2$ homolysis and the cyclization reaction eq 12 are competitive in the 850–1200 °C range where shock and impact initiation takes place. This would imply that the chemical reactions responsible for shock and impact initiation are not necessarily the same as those of slow, controlled thermolysis. In fact, Storm *et al.*[27] found TNT to be an outlying point in a plot of impact vs shock sensitivity for 21 explosives.

In conclusion, C–$NO_2$ homolysis, whether unimolecular as in the gas phase or assisted by intermolecular interactions as in the condensed phase, would appear to be a major early thermal decomposition reaction of nitroaromatic compounds at *high temperature*, probably above 900 °C. The role of this channel compared to C–$NO_2$ isomerization is difficult to assess in the condensed phase.

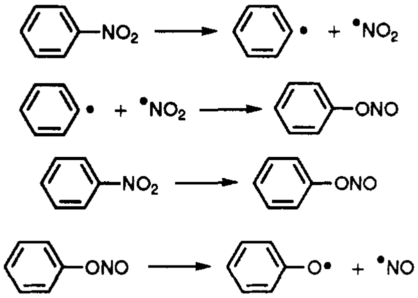
## B. Nitro–Nitrite Isomerization

Evidence of the nitro–nitrite rearrangement on an aromatic backbone exists primarily in the gas phase and in dilute solution. In the condensed phase of the bulk material, the evidence is more circumstantial. Unfortunately, no aryl nitrite compounds appear to have been isolated and characterized. Isomerization of C–$NO_2$ in the condensed phase could be very important relative to C–$NO_2$ homolysis.

In the gas phase the clearest evidence of the nitrobenzene-to-nitritobenzene isomerization comes from the fact that the thermal decomposition of nitrobenzene is insensitive to the presence of excess $NO_2$.[32] An estimate [33] of the rate constant for this rearrangement produces the Arrhenius plot shown in Figure 2. While this estimate shows that isomerization is never the fastest reaction, a small change in the assumed *A* factor alters the importance of the isomerization process relative to the other reactions in Figure 2. The isomerization reaction also has a small or negative volume of activation and, therefore, would be favored over unimolecular bond scission at high pressure.[120]

In the condensed phase, isomerization could be important because of its low volume of activation. Evidence of a reversible nitro–nitrite rearrangement involving a nitroaromatic compound exists in the $^1$H and $^{13}$C NMR spectra of 2,6-dichloro-4-methylphenol following nitration in chloroform.[121] Nitration occurs at the 4-position which makes this carbon atom formally sp$^3$ hybridized. The nitro–nitrite rearrangement, therefore, does not actually occur on an aromatic carbon atom. Nitro–nitrite isomerization has long been known to take place on an aliphatic carbon atom.[122]

Conspicuous circumstantial evidence for the nitro–nitrite rearrangement of nitroaromatic compounds in the bulk state is the fact that $NO_2$(g) is not observed or is, at most, a minor product of thermal decomposition below 500 °C.[123] Instead, a large quantity of NO is formed.[48,49,123–125] These observations have been cited as evidence of the different contributions of eqs 15, 16,[125] 17,[32,33,49,120] and 18.[33,49,125,126] As with eq 15 discussed in section IV.A, eqs 16–18 have been analyzed in the gas phase, but not in the condensed phase, where the details are more difficult to establish. Beynon *et al.*[127] were among the first to contribute to this area. They observed that pyrolysis of nitrobenzene at 600 °C produced NO and the phenoxy radical. Above 800 °C, shock tube studies[33] indicate that eqs 17 and 18 occur, while laser-powered pyrolysis reveals[32] that the nitrite forms by eq 17, rather than by eqs 15 and 16. However,



(15)

(16)

(17)

(18)

eq 15 is more than twice as prevalent as eq 17 above 800 °C.[33] The fact that these shock tube and laser pyrolysis studies were conducted at lower pressure would disfavor the bimolecular eq 16. Equation 16 would be expected to contribute importantly in the condensed phase.

Values of $E_a$ and the BDE for eq 15 are in the 65–72 kcal/mol range (section IV.A). Although the rate of isomerization by eq 17 has not been measured directly, it is likely to be slow on the basis of the estimate of a relatively high $E_a$ of 55.9 kcal/mol[33] and computational estimates.[120] The BDE of the O–NO bond in eq 18 is approximately 23.7 kcal/mol.[128] Taken together these results are consistent with eq 15 being the prevalent reaction at high temperature and low pressure.[33]

Reactions of the type shown in eqs 15–18 also appear to occur when other substituents are present on the aromatic ring. Fields and Meyerson[116] found ions in the mass spectrum consistent with eq 18 when 1,3- and 1,4-nitrotoluene and 1,3-dinitrobenzene decompose. The major pathway of decomposition of 3,4,5-trinitrotoluene ion by EI/MS is loss of NO, which was proposed to result from eqs 17 and 18.[39] Decanitrobiphenyl was speculated to decompose in solution through the isomerization steps, eq 17.[129] MNDO and MINDO/3 computations[130] on a model compound of TNT, 1-nitropropene, reveal that the transition state equivalent to eq 17 is favorable and is consistent with the formation of radicals by eq 18.

Considering the evidence available, concrete proof does not exist for nitro–nitrite isomerization of nitroaromatic compounds during thermal decomposition. However, circumstantial evidence is abundant. The isomerization (eq 17) could occur directly in the condensed phase, or at higher temperatures it could occur by eqs 15 and 16. A variation of eq 16, for which there is abundant evidence,[121,122,131] involves converting an sp$^2$ carbon to an sp$^3$ carbon and adding $NO_2$ at the sp$^3$ carbon atom. The copious amount of NO(g) formed upon thermolysis of nitroaromatic compounds is further evidence of eq 18. However, it is doubtful that all of the NO(g) generated by nitroaromatic compounds comes from eq 18. Other sources of NO(g) certainly exist. In addition to eq 18, NO(g) can be formed by thermal decomposition of HONO, which forms when $^\bullet NO_2$ abstracts H$^\bullet$. Most nitroaromatic compounds are abundant sources of H$^\bullet$.[61] Equation 19 occurs readily at the temperatures which nitrobenzene compounds thermally decompose. This route to NO(g) is indicated

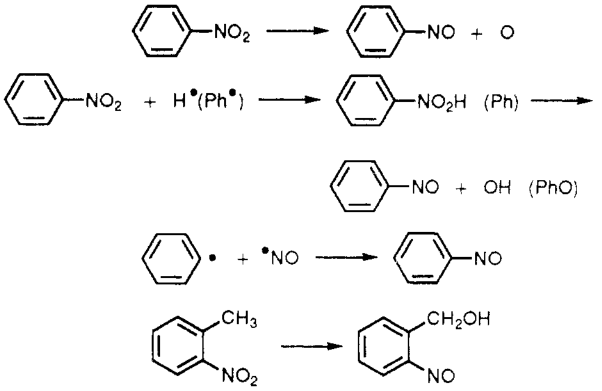
$$2HONO \rightarrow NO + NO_2 + H_2O \qquad (19)$$

to be unimportant during pyrolysis of nitrobenzene in one study,[69] but contributing in another.[125] Equation 19 has been mentioned frequently in the thermal decomposition mechanisms of substituted nitroaromatics.[33,36,48,130,132] A third source of NO(g) is thermal decomposition of nitrosoaromatic compounds that could form in the decomposition scheme of nitroaromatic derivatives (section IV.C). These reactions are described next.

## C. Formation of Nitrosoaromatic Intermediates

Kinetic measurements of the formation and thermal decomposition of nitrosoaromatic compounds from nitroaromatic compounds are not available. However, from a thermochemical point of view, the C–N BDE of nitrosobenzene is 50.8 ± 1 kcal/mol compared to nitrobenzene at 71.3 ± 1 kcal/mol.[133] On this basis, formation and reaction of nitrosoaromatic compounds is probably a lower temperature process than C–$NO_2$ homolysis. Any temperature at which C–$NO_2$ homolysis is facile would exceed the temperature required to cleave the C–NO bond.

As is the case for other reactions of the –$NO_2$ substituent described in sections IV.A and B, the clearest evidence of formation of the nitroso substituent from the nitro group exists in the gas phase. Equations 20–23 give several possible routes to the nitroso group.



(20)

(21)

(22)

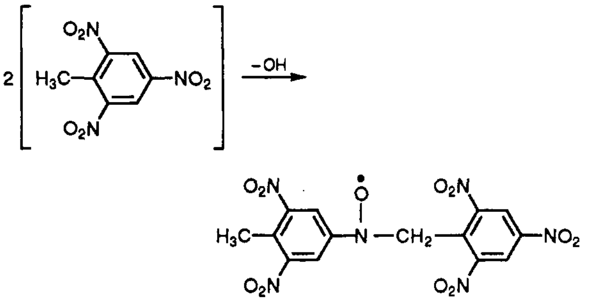
(23)

Equation 20 has been proposed to occur during pyrolysis of nitrobenzene in benzene solution at 275 °C where, after chromatography, nitrosobenzene is the major nitrogen-containing product.[49] Also, EI/MS[39] and MS/MS-CID[134] of TNT produces a major ion with $m/e$ = 211 corresponding to the loss of O.

Equation 21, in which an oxygen atom is abstracted by reaction with a radical, would be expected with a radical-producing substituent *ortho* to the –$NO_2$ group. Since it is a bimolecular reaction, eq 21 is potentially more important in the condensed phase. Equation 21 has been proposed to occur for nitrobenzene in benzene solution[49] and in the gas phase of TNT by EI/MS[39] and MS/MS-CID[134] where loss of OH produces the dominant ion.

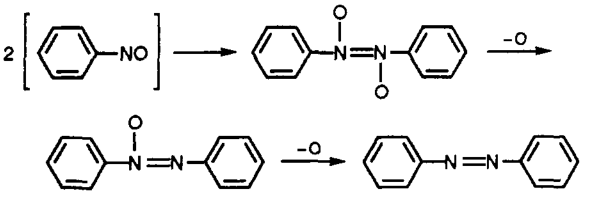
The fact that NO forms in high concentration when many bulk nitroaromatic compounds are pyrolyzed[48,49,123–125] makes eq 22 a probable source of nitrosoaromatic compounds by recombination in the condensed phase. Equation 23 has been analyzed computationally as a potential step in the decomposition of TNT.[135] MINDO calculations suggest that eq 23 is favored over H transfer from –$CH_3$ to –$NO_2$ to form the *aci*-isomer.[135] The same conclusion was reached from MNDO and MINDO/3 calculations of 1-nitropropene,[130] a model compound for TNT. Oxidative insertion of O into the CH bond has been speculated upon to be the RDS in thermal decomposition of TNT.[20]

The chemistry of nitrosoaromatic derivatives must be considered in the lower temperature decomposition schemes of nitroaromatic explosives, but probably not in shock initiation processes. Evidence for this comes from XPS studies of Owens and Sharma[136] who found evidence of the nitroso group in thermally decomposed TNT, but not in shocked TNT. Indeed, Adams *et al.*[137] isolated a toluene-soluble nitroso-containing compound proposed to be 2-nitroso-4,6-dinitrobenzyl alcohol from the thermal decomposition products of TNT. Thermal decomposition of TNT alone and in the presence of hexamethylbenzene produces a nitroxide radical that corresponds to condensation with loss of OH, eq 24.[138]



(24)

This radical is closely related to the nitroso compounds discussed above. Likewise, nitrosoaromatics can couple to form azoxy and azo compounds which have been isolated from the residue of TNT formed during 16 h at 200 °C.[20] Coupling of nitrosoaromatics to form azo and azoxy compounds is proposed in other studies.[139] Equation 25 is representative.



(25)

Decomposition of nitrosoaromatic compounds is a source of NO upon thermolysis. Both the nitrosobenzene ion[139] and the nitroso ions of TNT[134] produce NO by MS/MS-CID.

## D. Reactions of the $-NO_2$ Group with an *Ortho* Substituent

Numerous studies indicate that most polyatomic substituents positioned *ortho* to the $-NO_2$ group on the aromatic ring enhance the reactivity compared to *meta* and *para* positioning. Synthetic chemists have known of this fact since the 19th century. Reactions of substituents with an *ortho* $-NO_2$ group are now a widely used synthetic route to many heterobicyclic molecules.[140–142] Mechanisms of these reactions have been discussed.[140,143] Reactivity differences in relation to explosive properties began to be discussed in the early 20th century.[83,144] For example, 2,4,6-TNT self-ignites at about 210 °C, whereas 1,3,5-TNB is stable at 300 °C, indicating that $-CH_3$ somehow activates the molecule.

Clear illustrations of the generality of the "*ortho* effect" arise when classes of substituted nitrobenzene compounds are compared. The relative rates of thermal decomposition of 2-nitrotoluene, 3-nitrotoluene, and 4-nitrotoluene in the vapor phase at 200 °C are 400: 0.8:2.0.[96] The EI/MS and MS/MS-CID of these molecules differ significantly. 2-NT loses OH while 3-NT and 4-NT lose O, NO, and $NO_2$.[36,126] The $-CH_3 \cdots ON-$ intermolecular interaction clearly destabilizes the molecule.

Kinetic data for the gas-phase decomposition of a series of *ortho*-substituted nitrobenzene derivatives[102] in Table VIII are further evidence of the generality of the *ortho* effect. In all three compounds the primary deuterium isotope effect indicates that the H atom is transferred in the RDS of the reaction. $E_a$ for 2-NT in Table VIII is 10–20 kcal/mol lower than those in Table VII where the $C-NO_2$ homolysis occurs. Ions of all three compounds in Table VIII primarily fragment by loss of OH in the EI/MS and MS/MS-CID modes.[36,126]

**Table VIII. Gas-Phase Kinetic Data[102] for Nitrobenzene Derivatives Having *Ortho*-X Substitution**

| x | $T$, °C | $k_H/k_D$ | $E_a$, kcal/mol |
|---|---|---|---|
| $CH_3$ | 350–420 | 1.54 | 49.5 |
| $NH_2$ | 400–470 | 1.48 | 57.5 |
| OH | 390–460 | 1.75 | 52.4 |

The reactions between $-NO_2$ and *ortho*-related substituents profoundly affect the thermal decomposition chemistry and explosive properties of polynitroaromatic explosives. Individual substituents are now considered by category.

### *1. α-CH Bonds*

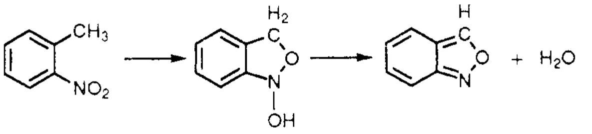
The number of clear indications are overwhelming that an α-CH bond *ortho* to $-NO_2$ on an aromatic ring activates the thermal decomposition process.[5,20,21,24,33,34,39,51,53,86,96,126,132,134,140,145–147] That an alkyl group plays a fundamental role in thermal decomposition is not at all surprisingly when these compounds are viewed as a subclass of hydrocarbon chemistry. The RDS in the oxidation of hydrocarbons in the liquid phase involves C–H scission.[148] The C–H bond of an alkyl group is more reactive than a C–H bond of an aryl group.[148] However, for destabilization of the nitrobenzene fragment, it is not simply the presence of an *o*-alkyl group that counts. The presence of an α-CH bond in the *o*-alkyl group is the most significant factor. Evidence for this is the fact that at 200–260 °C in the melt phase, 2,4,6-TNB substituted by $-CH_3$, $-CH_2CH_3$, and $-CH(CH_3)_2$ decomposes at about the same rate, whereas $-C(CH_3)_3$ substitution produces a 30–50 times slower rate.[86] However, following α-CH abstraction the reaction sequences for this series of compounds are very different.[37]

Insight that a nitroaromatic compound becomes activated by *ortho* $-CH_3$ substitution came to light nearly a century ago when 2-NT appeared to condense to anthranil, eq 12, upon heating.[149–151] In particular, 2-NT heated in aqueous or alcoholic base rearranged to anthranilic acid,[149–151] which is the hydrolysis product of anthranil. Likewise, Fields and Meyerson[116] recovered methylanthranilate when 2-NT in $CH_3OH$ was heated to 600 °C in a Vycor tube for 11 s. The mechanism of this reaction has been discussed.[65] Because these reactions occur in the condensed phase, the role played by bimolecular processes and wall effects is unknown. These perturbations are eliminated by the use of a single pulse shock tube.[33,34] The kinetics and products of unimolecular thermal decomposition of 2-NT reveal that eq 12 is the dominant reaction pathway, at least below about 900 °C.[33,34] Previous kinetic studies of 2-NT using the rate of gas evolution[96,102] and these shock tube data are given in Table IX. The Arrhenius factors are smaller than those for $C-NO_2$ homolysis (Table VIII). The relatively low *A* factor suggests that a tight transition state exists, which is expected of a cyclic activated complex collapsing to

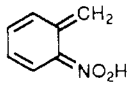
**Table IX. Arrhenius Data for Condensation of 2-Nitrotoluene to Anthranil (Eq 12)**

| *T*, °C | $E_a$, kcal/mol | *A*, $s^{-1}$ | ref |
|---|---|---|---|
| 300–350 | 42.5 | $10^{10.22}$ | 96 |
| 400–450 | 49.5 ± 1.3 | $10^{12.4\pm0.4}$ | 102 |
| 797–907 | 51.520 | $10^{13.08}$ | 33 |

a closed ring.[34,84] Indeed, $\Delta S^\ddagger$ is −15 cal/deg for 2-NT compared to 20 and 14.5 cal/deg for 3-NT and 4-NT.[96] As described in section IV.A, 3-NT and 4-NT thermally decompose by C–$NO_2$ homolysis which produces a positive $\Delta S^\ddagger$. The clear experimental evidence that 2-NT condenses to anthranil upon heating is supported by the relative energies determined by *ab initio* SCF-MO methods.[152] The bicyclic tautomer intermediate and the anthranil product of eq 26 form exothermically and thus are thermodynamically favored relative to 2-NT. The first step of eq 26 is suggested by UV photolysis of 2-NT which produces a short-lived *aci* tautomer, I.[153-156] I is a variation on the intermediate species in eq 26. SCF-MO calculations on TNT at the STO-3G level indicate that the barrier to H transfer when forming the TNT equivalent of I is 54 kcal/mol,[157] which is 4–13 kcal/mol larger than the global induction phase activation energy of TNT (Table V). An earlier MNDO calculation on TNT concluded[135] that intramolecular H transfer to form I was less likely than O insertion into the CH bond by eq 23. However, the SCF-MO model is more dependable for assessing the relative energy of these processes. Elsewhere the MNDO model of 1-nitropropene indicated that H transfer from $-CH_3$ to $-NO_2$ is energetically favorable.[130] This result is consistent with the SCF-MO results.



(26)

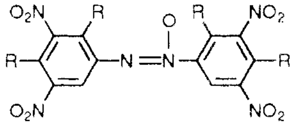


I

The experimental and computational results for 2-NT are useful guides to the possible behavior of TNT. However, 2-NT is only a model of an explosive and has been studied primarily in the gas phase. From the point of view of a true explosive, the behavior of the bulk material in the condensed phase must be understood. Consequently, the unimolecular reaction conditions of the gas phase need to be modified to account for bimolecular reactions and catalysis that are important in the condensed phase. Condensed-phase decomposition is further complicated by the fact that H atoms are such important participants in the decomposition of TNT.[61,158] The rate of H transfer is fast, being less than 3.1 μs in solution.[156] Consequently, many H-atom transfer steps can occur in a very short time at temperatures below 300 °C where most decomposition studies of polynitroaromatic explosives are conducted. Moreover, O transfer occurs under certain conditions in the condensed phase.[159]

TNT melts at 81 °C so that studies of condensed-phase decomposition almost always refer to the molten state. Several studies report separation and identification of products in an attempt to determine how the methyl group activates thermal decomposition. Many products are possible because all of the oxidized forms of $-CH_3$ and reduced forms of $-NO_2$ are present and each displays its own intermolecular and intramolecular chemistry. Consequently anthranil, alcohol, aldehyde, carboxylic acid, nitroso, oxime, nitrile, nitrone, nitroxide, azo, and azoxy groups form.[20,21,137,139,160-162] Disruption of the aromatic ring also occurs, leading to gas products including NO, CO, $CO_2$, $N_2$, and $H_2O$.[87,137] An insoluble high molecular weight "explosive coke" having the elemental composition of $C_6H_3N_2O_{3.75}$ forms from TNT.[137] All of these products result from "cooking" reactions and, as such, cannot be attributed with confidence to the initiation or explosion chemistry of TNT. However, several useful results emerge from this work and are discussed next.

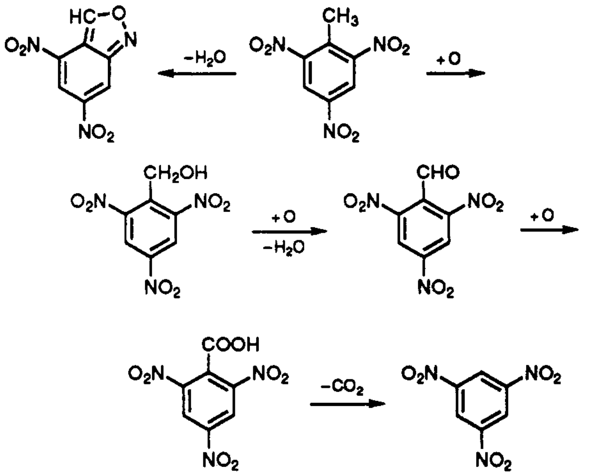
Rogers[21] used thin-layer chromatography to separate the products formed by programmed heating of TNT at 300 °C. 1,3,5-TNB, 2,4-DNAn, 2,4,6-trinitrobenzyl alcohol, and 2,4,6-trinitrobenzoic acid were isolated from a large quantity of unreacted TNT. He propose that oxidation of $-CH_3$ to $-CH_2OH$ is the first step. Dacons *et al.*[20] heated TNT for 16 h at 200 °C in a loosely capped vial. About 25 benzene-soluble compounds were extracted from the dark brown residue. An insoluble residue included the "explosive coke" reported by Adams *et al.*[137] Unreacted TNT constituted 75–90% of the material. The same benzene-soluble products found by Rogers[21] (except for TNB) were obtained, but, in addition, 2,4,6-trinitrobenzaldehyde and dimeric reduction products suspected of containing the azo and azoxy linkages (II) were found.



II

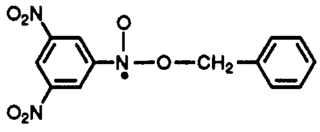
None of the products amounted to more than 1% of the original quantity of TNT. Neither Rogers[21] nor Dacons *et al.*[20] analyzed the gases formed, but Rogers noted that only a few percent of the weight is lost. Consequently, most of the decomposition reactions produced products with low volatility. It is not surprising that the products in these two studies differ somewhat because of the different reaction temperature. While Dacons *et al.*[20] stress the importance of these differences, Rauch *et al.*[163-165] repeated this work by using TNT heated at 275 °C, which is intermediate between the temperatures used by Rogers[21] and Dacons *et al.*[20]. Products common to both studies were isolated indicating that the main factor in the product differences was simply the reaction temperature. After merging the results of these cooking degradation studies, the presence of successive oxidation products of the $-CH_3$ group, eq 27, is conspicuous. All of these products also appear in the synthesis of TNT.

Many of the products discussed above are formed from TNT because of the relatively low decomposition temperature and the long reaction time. It is unlikely that they all are present or contribute significantly during rapid decomposition where the reaction times are shorter and the temperature is higher. As has

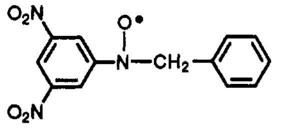


(27)

already been emphasized, high temperature favors higher $E_a$ and more endothermic processes. Therefore, experiments designed to specify individual steps or to control the conditions more precisely require interpretative care if the goal is to define the decomposition process of TNT under other conditions. For example, a low $E_a$ process is revealed by ESR spectroscopy during UV photolysis of TNB in toluene at 200 K. The primary radical is III which converts with time or on heating to two conformers of IV.[166] Caution must be exercised

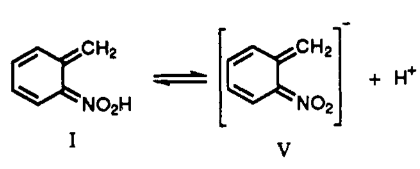


III



IV

when using these results to understand TNT decomposition because these are low $E_a$ processes. Moreover, Davis *et al.*[167] found that the radical formed by photolyzing TNT in diethyl ether is not the same as those formed by heating TNT. On the other hand, there is absolutely no doubt about the ease by which an H atom can migrate from the $-CH_3$ group of TNT. In solution, UV photolysis gives evidence of H atom transfer to give I,[153–156] which equilibrates, in the case of the TNT equivalent, with the trinitrobenzyl anion (V) (eq 28).[145,156] Lewis bases, such as $OCH_3^-$ and



(28)

$OC_2H_5^-$, abstract $H^+$ from the $-CH_3$ group of TNT[158,168] to produce V. V is highly reactive and, as the TNT equivalent, couples to produce HNS[169] under appropriate conditions. In the gas phase, the dominant fragmentation step of TNT and 1,3,5-trinitroxylene is loss of OH.[39,126,132,134,170] For this to occur H atom transfer to $-NO_2$ followed by $-N(O)-OH$ homolysis must be the dominant initial decomposition step of the isolated molecule. In fact, all TNT isomers, except 3,4,5-TNT, fragment by loss of OH.[146]

Solid evidence of C–H bond scission from the $-CH_3$ group of neat TNT exists in the primary deuterium isotope effect observed by DSC during the induction phase (Figure 1) of TNT and TNT-$\alpha$-$d_3$.[51] A primary isotope effect indicates that C–H bond scission occurs in the RDS. Shackelford *et al.*[51] proposed that a single unidentified catalyst promotes the reaction rate in the induction phase. They were apparently unaware of the earlier report of Maksimov *et al.*,[59] who suggested that 2,4-DNAn or 2,4,6-trinitrobenzaldehyde (eq 27) was the catalyst. Maksimov *et al.*[59] found that a 9:1 TNT/2,4-DNAn mixture reproduced the acceleratory decomposition characteristics of TNT. 2,4,6-Trinitrobenzaldehyde was shown previously to catalyze the decomposition of TNT.[20] In reality it is very difficult to specify the catalysts of decomposition of TNT with certainty. Robertson[44] found that the decomposition rate of TNT was accelerated by all 25 compounds that he added. Molecules that are able to produce $H^•$ catalyze the decomposition.[51] Unfortunately, ample concentrations (e.g. $10^{-4}$ M) of such species appear at relatively low temperature when neat TNT is heated.[61]

Whether it is intra- or intermolecular $H^•$ transfer that produces the *aci*-tautomer of TNT (I) and starts the decomposition chain is more of academic mechanistic interest than practical importance. However, some studies emphasize intra- or intermolecular H transfer[48] to the exclusion of the other. Considering all of the literature together, there is little doubt that, when both are possible, both will contribute. In solution and in the gas phase at low pressure, unimolecular $H^•$ transfer dominates.[32,34,36,37,96,102,116,155,156] If the pressure is raised in the vapor phase, the decomposition of TNT shifts from unimolecular at lower pressure to bimolecular at higher pressure.[53] In the face of this result it is interesting that the decomposition rate of molten TNT is independent of pressure up to 50 kbar.[171] This has been attributed to the fact that the volume of activation of 2,4-DNAn is similar to that of TNT.[172] On the other hand, it could mean that intermolecular association and $H^•$ transfer or even C–$NO_2$ to C–ONO isomerization dominate at all pressures studied.

Evidence of significant intermolecular association of polynitrobenzene molecules in the condensed phase that would facilitate intermolecular $H^•$ transfer appears in many forms. The crystal structure of TNT[173,174] reveals that intramolecular and intermolecular $H^•$ transfer may be equally probable in the condensed phase. The intermolecular –CH···OH– distances (2.39–2.62 Å) are very similar to the intramolecular distances (2.38–2.70 Å). Structural details of the solid phase do not necessarily carry over to other phases, but the vibrational spectra of TNT in the solid, liquid, and vapor state are similar.[174–177] This suggests that the intermolecular –CH···ON– distances in the solid are similar to those in the melt where decomposition occurs. The large amount of intermolecular association in the melt is responsible for the unusually high Trouton's ratio $\Delta H_v/T_b$ of 23–33 cal/(deg mol)[48] for polynitrobenzene compounds compared to about 22 cal/(deg mol) for weakly associating molecules. Aggregates of nitrobenzene molecules exist even at 350 °C.[178] The *A* factors for thermal decomposition of many polynitroaromatic compounds[48] are in the range of $10^5$–$10^{10}$ s$^{-1}$ which is smaller than the lower limit of unimolecular reactions of about $10^{12}$ s$^{-1}$. The negative $\Delta S^‡$ for some of these reactions is suggestive of an ordered transition state.[34] An energetically stable transition state forms by intermolecular $H^•$ transfer from $-CH_3$ to $-NO_2$ according to MNDO and MINDO/3 MO calculations on 1-nitropropene.[130] Finally, the mere fact that the rate of thermal decomposition of TNT is about 10 times faster in the melt than in the vapor phase[48] is reasonable evidence of the importance of intermolecular H$^\bullet$ transfer in the condensed phase. However, this latter observation could also be attributed to catalysis by the decomposition products.

C–H bond scission from the $-CH_3$ group of TNT, although not unimolecular, appears to play a practical role in the sensitivity and explosive properties of polynitroaromatic explosives in the bulk state. The explosive properties of interest include the sensitivity to impact and shock initiation. As discussed in section II.A, impact sensitivity is determined by the drop-weight impact test and is governed to a large extent by thermal decomposition processes.[1,2] In accordance with this notion, log $H_{50}$ for polynitroaromatic compounds is found to correlate with the oxidant balance,[24] the reducing and oxidizing valencies of the composing elements,[179] the molecular electronegativity,[180] and the polarity of the $C-NO_2$ bond in the ground and excited states[117]. Particularly interesting results are those of Kamlet and Adolph[24] and Bliss *et al.*,[181] who found a statistically significant separation of log $H_{50}$ vs $OB_{100}$ for nitroaromatic explosives into two families. With several exceptions the distinguishing feature is the presence or absence of an $\alpha$-CH bond *ortho* to $-NO_2$. Compounds with $\alpha$-CH bonds were more sensitive to impact. Bliss *et al.*[181] noted that this separation may merely result from dilution of $OB_{100}$ by the $CH_3$ group. Bulusu and Autera[66] noted a small deuterium isotope effect in the shock sensitivity (1.09–1.14) and detonation velocity (1.04–1.06) when TNT was compared to TNT-$\alpha$-$d_3$. This observation suggests that $\alpha$-CH bond scission might have some role in shock initiated chemistry and in steady detonation. Consistent with this is the fact that the shifts of the N(1s) and O(1s) XPS peaks in shocked TNT have been interpreted as showing migration of H toward O.[136]

All of the observations in the foregoing paragraph are phenomenological in that they suggest a role for the $\alpha$-CH bond in the explosive properties, but do not give a mechanism. In some cases different processes produce the same effect. The primary kinetic isotopic effect ($k_H/k_D = 1.66 \pm 0.2$) found for the decomposition of TNT over minutes at 263 °C is likely to be caused by the formation of 2,4-DNAn or a related compound.[51] The small values for the deuterium isotope effect observed for shock initiation and the detonation velocity[66] could result from dilution of the C–H bond rupture channel by the $C-NO_2$ homolysis channel. Shock initiation and the velocity of detonation are dominated by reactions in the submicrosecond time and the higher temperature regime. In this regime an isotope effect can also arise from the transport rate differences of H and D (1:1.4). Therefore, the small isotope effects observed may be caused by transport rate differences mixed with C–H homolysis chemistry and diluted by $C-NO_2$ homolysis. Furthermore, polynitroaromatic compounds containing $\alpha$-CH bonds are not distinguishable from other compounds when the detonation pressure and $E_a$ of slow thermal decomposition are correlated.[7] In fact, Kamlet and Hurwitz[182] do not believe that reaction kinetics even influences the velocity of detonation at infinite diameter.

The overall description of the decomposition process of neat TNT in relation to its explosive characteristics requires both kinetic and mechanistic footing. The following view of TNT[87] rests on firm ground based on the foregoing discussion.

a. *The dominant initiating processes of TNT are $-CH_3$ oxidation producing 2,4-dinitroanthranil, 2,4,6-trinitrobenzaldehyde, etc.; $C-NO_2$ homolysis; and catalyst-dominated chemistry.* Validation of this statement emerges from consideration of the kinetic and the mechanistic discussions above. The global reaction rates for the induction, acceleratory, and decay phases of TNT below 400 °C were given in Table V, and for nitrobenzene and nitrotoluene derivatives in Tables VI, VIII, and IX. With these data the reaction time at a given temperature can be assessed for these main classes of reactions. $E_a$ values in Table V for the induction phase of TNT are 41–51 kcal/mol, whereas for anthranil formation from 2-NT in Tables VIII and IX, $E_a$ is the range of 42.5–51.5 kcal/mol. This overlap is reasonably good evidence that the rate of the induction phase reactions of bulk TNT below 400 °C is dominated by the formation of 2,4-DNAn and compounds closely related to it. Moreover, there is virtually undisputable augmenting mechanistic evidence discussed above that both intra- and intermolecular H$^\bullet$ transfer from $-CH_3$ to $-NO_2$ initiate thermal decomposition of TNT below 400 °C. To represent the rate of this induction phase process in bulk TNT, the $E_a$ and $A$ values of Cook and Abegg[79] are useful because they are carefully determined and are about the average of the data available (Table V).

As discussed in section IV.A, $C-NO_2$ homolysis is the dominant initial reaction of nitrobenzene compounds above about 900 °C. To assess this reaction in TNT, the rate data for 1,3,5-TNB in Table VI are valuable.

Finally, for the acceleratory phase, the global rate data reflect the effects of catalysis on the numerous reactions that take place in this stage. The dominant reactions are unknown, but catalysis is an important factor in the rate. The rate data of Robertson[44] in Table V are useful for representing this phase. These three processes lead to conclusion b.

b. *The proper description of the dominant initiation reaction of bulk TNT depends on the temperature and reaction time.* This statement follows from consideration of the relative importance of the three reaction catagories highlighted in *a* in terms of the time required to complete the reaction at a given temperature. This can be assessed by eq 29. Figure 4 is a plot

$$T_{rxn} = \frac{E_a}{R\,(\ln A + \ln \Delta t)} \tag{29}$$

of the results. Note that the rate of the bulk phase induction reaction corresponding to the formation of 2,4-DNAn and the oxidation of $-CH_3$ matches the rate of $C-NO_2$ homolysis at about 770 °C. Above 770 °C $C-NO_2$ homolysis is the faster reaction, while below 770 °C, the $-CH_3$ oxidation reaction is faster. The reaction time at this crossover temperature is about 1 ms. Consequently, the impact sensitivity which results in heating for about 250 μs might be expected to be influenced by reactions of the $-CH_3$ group, as Kamlet

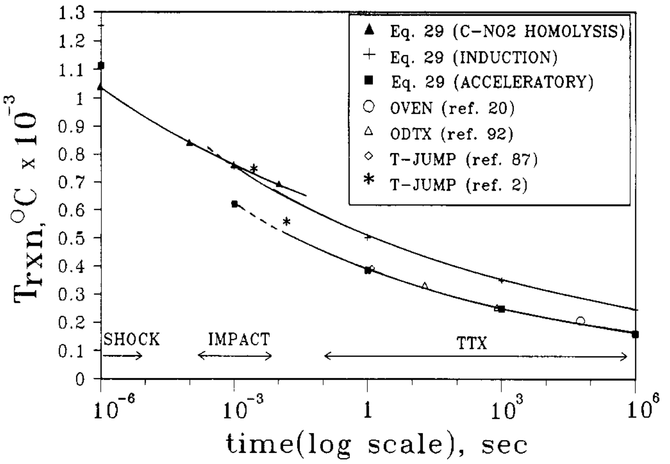


**Figure 4.** Times-to-explosion for TNT modeled with rate constants of three processes: C–$NO_2$ homolysis, –$CH_3$ oxidation (induction phase), and catalysis by decomposition products (acceleratory phase).

and Adolph[24] and Bliss *et al.*[181] found. However, for shock sensitivity, in which the full energy input occurs in about 1 μs or less and $T \geq 1000$ °C, C–$NO_2$ homolysis contributes more than the –$CH_3$ group oxidation. It is, therefore, understandable why the deuterium isotope effect[66] is diluted, because C–$NO_2$ homolysis has become very important. The fact that the impact sensitivity, $H_{50}$, is more influenced by –$CH_3$ group oxidation, while the shock sensitivity, $P_{90}$, is more influenced by C–$NO_2$ homolysis, is the probable reason why TNT is an outlying point on a plot of $H_{50}$ vs $P_{90}$ for a series of explosives.[27]

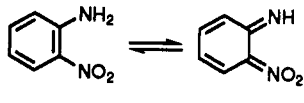
c. *The time-to-explosion of TNT at times longer than 0.1 s is controlled by catalytic reactions of the acceleratory phase. Shorter thermal explosion times are also influenced by C–$NO_2$ homolysis and –$CH_3$ oxidation.* Experimental times-to-explosion measured in different ways over eight logarithmic decades of time are given for TNT in Figure 4. Notice that between 1 and 60 000 s the time-to-explosion is not modeled by the induction phase kinetics of Table I, as might be expected, but rather by the acceleratory phase kinetics which reflects catalysis. At shorter reaction times ($10^{-2}$–$10^{-3}$ s) the time-to-explosion departs from the acceleratory phase kinetics. This could simply be the result of experimental inadequacies, such as the inability to achieve efficient heat transfer, that place the measured temperature higher than the true sample temperature. Acknowledging the experimental shortcomings, the time-to-explosion in Figure 4 at short times departs toward the induction phase rate and the C–$NO_2$ homolysis rate and away from the catalytically dominated acceleratory phase rate. Hence, at short reaction times primary reaction steps increasingly determine the time-to-explosion. However, at longer reaction times, catalysis and secondary reactions dominate the time-to-explosion. It is no surprise, therefore, that $E_a$ values from time-to-explosion measurements do not correlate with the molecular structure and elementary reaction kinetics of polynitroaromatic compounds.

### 2. α-NH Bonds

The difficulty of correlating the explosive characteristics of *o*-aminonitrobenzene compounds with their molecular and crystal features was described in section II.D. The amino group stabilizes the nitroaromatic molecule toward shock[67] and impact[24,181] sensitivity, but hexanitrobiphenyl explosives are exceptions in that the impact sensitivity is actually increased by the presence of –$NH_2$.[183] In these latter compounds, steric demands may weaken several of the C–$NO_2$ bonds. In reality, many variables change when –$NH_2$ groups are added to the trinitrobenzene backbone making it unlikely that a single parameter holds the key to the dramatic changes in the chemical and physical properties through the series TNB, MATB, DATB, TATB. The differences are partly due to the crystal structure and partly due to the molecular and electronic structure. The important features of the crystal structure are considered first.

Structurally, TNB, MATB, DATB, and TATB are very different. The intermolecular bond distances were given in Table III. TNB contains both planar and nonplanar benzene rings with –$NO_2$ groups twisted and bent out the plane and O atoms with large thermal parameters.[68] The –$NO_2$ groups of MATB are noncoplanar with the benzene ring.[69] The dihedral angles are 22.5°, 4.0°, and 8.5°. Curiously, the most rotated –$NO_2$ group is 2-$NO_2$ which might have been expected to be coplanar because of intramolecular hydrogen bonding. Instead, intermolecular hydrogen bonds force this –$NO_2$ group out of the plane. From the point of view of the structure alone DATB[70] and TATB[71] are relatively similar. Both molecules are planar with chainlike intermolecular hydrogen bonding in DATB and layerlike bonding in TATB. Interplanar π-electron interactions exist.

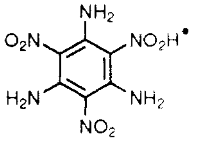
Electronically, the presence of the –$NH_2$ and –$NO_2$ substituents on an aromatic ring produces intricate competitive effects. The –$NH_2$ group is inductively withdrawing but resonance donating of electron density, whereas the –$NO_2$ group is both resonance and inductively withdrawing. Therefore, it is difficult to predict the reactivity of the ring when both groups are present. Politzer *et al.*[184] and Rogers *et al.*[67] addressed this problem computationally. The addition of an –$NH_2$ group in the *ortho* position of nitrobenzene stabilizes the ring because of resonance. Accordingly, the C–$NO_2$ bonds become progressively shorter as the number of –$NH_2$ groups increases (Table III). SCF-3-21G MO calculations[185] reveal that the energy minimum for the *aci*-tautomer (VI) is higher than that of 2-nitroaniline.



VI

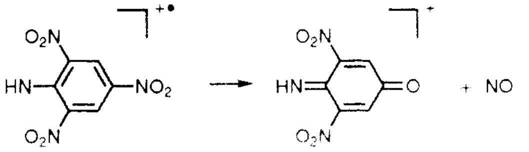
However, a significant body of experimental data is at odds with these computational findings. First, Matveev *et al.*[102] observed a primary deuterium isotope effect (Table VIII) in the gas phase when 2-nitroaniline and 2-nitroaniline-$d_2$ thermally decompose. This indicates that N–H bond scission, possibly of the type shown by VI, occurs in the RDS. $E_a$ for the decomposition step is relatively large (57.5 kcal/mol) which necessitates a relatively high temperature for the reaction to occur at a rapid rate. This temperature is still below that of other plausible reaction routes, such as C–$NO_2$ homolysis for which the $E_a$ values are 65–70 kcal/mol (Tables

VI and VII). Second, the principal mass spectral fragmentation step of 2-nitroaniline derivatives is loss of OH.[36,126] This fact strongly suggests that H transfer as in VI is facile. Third, ESR spectra of irradiated TATB produces long-lived radicals consistent with structure VII, which is proposed to form from intermolecular H$^\bullet$ transfer.[186,187] In view of positive evidence for species or processes involving or formally resembling VI in either the transition state or as a stable species, the negative computational evidence[185] evokes skepticism. More consistent with experiment is the computational finding that conversion of 2-nitroaniline to benzofurazan by eq 14a is nearly thermally neutral.[27,152] There is substantial experimental evidence discussed below for these conversions when $-NH_2$ and $-NO_2$ groups are *ortho* related.



VII

Equation 14a has been known for at least 80 years, and eq 14b is especially prevalent in an oxidizing environment.[188,189] These reactions are standard in organic synthesis.[141,190] In addition to the primary deuterium isotope effect when 2-nitroaniline decomposes,[102] Rogers *et al.*[191] found a primary isotope effect ($k_H/k_D$ = 1.5) when TATB thermally decomposes at 297–382 °C. These findings support eq 14 as the lower temperature decomposition channel. The unimolecular decomposition of MATB is a straightforward extension of the behavior of 2-nitroaniline in that it loses OH by MS/MS-CID.[126] However, in addition to the potential for cyclization reactions, eq 14, MATB also loses NO from the radical cation produced by CID.[126] The mechanism is proposed to be eq 30, whose product is resonance stabilized. Furazan and furoxan formation occurs with TATB that has been thermally decomposed and subcritically shocked or impacted.[162,192–194] At least three different furazans were extracted by TLC and analyzed by CI-MS when TATB was thermally decomposed.[192] Curve resolution of the XPS line shapes of TATB subjected to shock and impact are consistant with formation of about 6% furazan and 6% furoxan derivatives.[193] On the other hand, there is no IR evidence of the furazan ring in thermally decomposed TATB.[195]



(30)

**Table X. Arrhenius Data for Thermal Decomposition of Amino-2,4,6-Trinitrobenzene Compounds**

| compound | phase | $T$, °C | $E_a$, kcal/mol | $A$, $s^{-1}$ | ref |
|---|---|---|---|---|---|
| MATB | gas | 301–343 | 38.5 | $10^{8.8}$ | 53 |
| | gas | 240–280 | 41.8 | $10^{11}$ | 84 |
| | liquid | 240–280 | 32 | $10^{7.2}$ | 84 |
| | liquid | 249–259 | 48 | | 54 |
| DATB | liquid | 320–323 | 46.3 | $10^{15.07}$ | 12 |
| | liquid | | 50 | $10^{15}$ | 58 |
| | solid | 220–270 | 47 | $10^{13.2}$ | 58 |
| TATB | gas/solid | 250–300 | 43 | | 196 |
| | solid | 297–382 | 59.1 | $10^{18.57}$ | 191 |
| | solid | 331–332 | 59.9 | $10^{19.5}$ | 12 |
| | solid | 345–375 | 62 ± 4 | $10^{19}$ | 197 |

Kinetics information on MATB, DATB, and TATB in the solid, liquid, and gas phase is compiled in Table X. Data for several alkylamine derivatives of 2,4,6-trinitrobenzene are not shown but are available.[54] The tendency for these compounds to react by eq 14 is the most logical explanation for the much smaller values of $E_a$ and $A$ compared to TNB (Table VI). Unfortunately, further analysis is necessarily qualitative because of scatter in the data and the fact that the measurements were made by different methods (DTA, DSC, manometry, electron beam heating traces, and effusion cell mass spectrometry). In the liquid and solid phase, matrix effects and catalysis by the decomposition products influence the Arrhenius constants (section II.C). There is a rough pattern of increasing $E_a$ and $A$ from MATB to TATB, which is consistent with the decrease in impact sensitivity along this series (Table I). However, the Arrhenius factors of TNB are clearly out of line because the initiation process ($C-NO_2$ homolysis) is different from eq 14. To analyze the relative roles of $C-NO_2$ homolysis and furazan/furoxan cyclization in the aminonitrobenzene series, the gas-phase data for MATB in Table X are perhaps least encumbered by matrix effects and catalysis. These rate data are compared in Figure 3 to that of TNB in Table VI.[198] The temperature at which $C-NO_2$ homolysis equals cyclization is 475 or 625 °C depending on the MATB rate chosen. Of course, these are isokinetic temperatures for the gas phase. Their relevance to the condensed phase is uncertain. If trusted, these temperatures are easily achieved in the condensed phase during shock and impact where Wenograd[2] estimated that TNB reaches 1060 °C in about 250 $\mu$s. Estimates of the isokinetic temperatures using the other data in Table X for MATB, DATB, and TATB produce unreasonably larger temperatures or impossible negative temperatures. Consequently, the temperature at which $C-NO_2$ homolysis becomes competitive with cyclization is uncertain for these compounds. However, Owens *et al.*[73,74] and Murray *et al.*[75] proposed that characteristics of the $C-NO_2$ bond are the main or rate-controlling factor in the shock and impact sensitivity. This is the only initiation reaction that TNB, MATB, DATB, and TATB could have in common to account for the smoothly increasing trend of impact sensitivity (Table I). The observation of furazan and furoxan compounds in heated, impacted, and shocked samples of TATB[162,192–194] is understandable from the fact that the temperature during heat-up and cool-down emphasizes the lower $E_a$ cyclization channel. The shocked and impacted samples did not explode and, therefore, did not reach the temperature range where $C-NO_2$ homolysis could dominate. Essentially the same spectral features subsequently interpreted as furazan and furoxan formation[162,192–194] were previously interpreted as evidence of $C-NO_2$ homolysis.[119,200]

$C-NO_2$ homolysis lacks appeal as the *source* of the decrease in shock and impact sensitivity as $-NH_2$ groups are added. This is because the $C-NO_2$ BDE is not especially sensitive to the other substituents on the ring (Tables VI and VII).[32,52] Thus, while $C-NO_2$

homolysis is one of the few common chemical initiation processes possible in TNB, MATB, DATB, and TATB, the increase in the amount of inter- and intramolecular hydrogen bonding along this series is a structural variable that may influence the shock sensitivity. These interactions have been proposed by Rogers *et al.*[67] to absorb shock energy and prevent it from being localized in the molecule. This effect is difficult to judge kinetically, but it could be accommodated in theories of how mechanical energy converts into chemical processes.[14-19] Raman spectroscopy of TATB during dynamic shock loading also suggests that the N–H···O bond becomes compressed.[35] A qualitative indication of the increase in the cohesive force in the lattice as $-NH_2$ groups are added is the increase in melting points (Table II). Any explanation of how hydrogen bonding controls shock and impact sensitivity must account for the fact that the chemical reactions begin at defects in the lattice (hot spots) and not in the homogeneous repeating lattice.

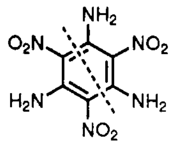
Taken together, the cyclization reactions (eq 14) of aminonitrobenzene explosives dominate the initial thermal reactions in the lower temperature range. These reactions could be important in sensitizing a "rough handled" explosive.[78] At high temperatures characteristic of shock and impact initiation, $C-NO_2$ homolysis appears to play a large and perhaps even dominant role in the initiation chemistry. A suit of products form quickly as a result of this homolysis reaction. The relative concentrations are determined by the temperature. These early species also influence the sensitivity and explosion characteristics.[198] Further thoughts on this stage of processes are given in section IV.

TATB is the most important explosive of this category and, as such, deserves further comment. TATB is infamous for its high thermal stability (>300 °C), low impact and shock sensitivity, and low solubility. The $C-NH_2$ bonds are unusually short [1.319(7) Å], while the C–C bonds are unusually long [1.444(7) Å] compared to C–C of benzene (1.40 Å)[71]. A typical C–C single-bond distance is about 1.47 Å. The $\pi^*$ MO's of the ring are partially occupied.[67] Strong intramolecular NH···O hydrogen bonding leads to a planar molecule while moderate intermolecular hydrogen bonding and interplanar $\pi$-electron interaction cause stacking of the molecules in graphite-like layers.[71,201]

Given the unusual materials properties of TATB and the significant amount of intermolecular association, complexity in the decomposition behavior is no surprise. Unlike most nitroaromatic explosives, TATB decomposes from the solid phase unless it is heated rapidly.[197] A melting point of about 450 °C has been mentioned,[197] although Meyer[13a] gives 350 °C, Bell *et al.*[183] give 330 °C, and Zeman[202a] gives 321–326 °C. Discoloration rather than melting is visually observed when TATB is heated at 2000 °C/s to 500 °C on a Pt filament; hence, the *rate* of melting is slow. Catalano *et al.*[45,195,202b] made numerous observations and measurements on the slow thermal decomposition of TATB. Reactions resulting in melting, formation of a residue, and release of gaseous products occur simultaneously with sublimation in the 305–357 °C range.[65] By DSC, the process is exothermic despite the fact that $\Delta H_{vap}$ is endothermic by 40 kcal/mol.[203,204] Perhaps five processes occur at 342–357 °C necessitating the use of multiple rate expressions.[45] The initial stage is autocatalytic with $E_a$ = 50–60 kcal/mol and appears to consist of at least two consecutive reactions. The global reaction order is 0.5. The overall $E_a$ resembles the values given in Table X. The remaining stages of decomposition have $E_a$ values in the range[3] of 50–80 kcal/mol.

MS and IR analyses of the gaseous products from confined and unconfined TATB suggest[202b] that the removal of intercalated $CO_2$, acetone, $H_2O$, and $N_2$ occurs initially. Approximately 1–2% of the space between the layers is occupied by these trapped molecules. It is conceivable that the small amount of $H_2$ also observed comes from furoxan formation, eq 14b, while some of the $H_2O$ may result from furazan formation, eq 14a. As the reaction rate accelerates into an explosion $CO_2$, $H_2O$, and $N_2$ increase in concentration and are joined by HCN, CO, and NO. Other gaseous products detected in small amounts included $N_2O$, $NO_2$, $CH_4$, and $C_2N_2$. A solid residue containing C, H, N, and O remained. The gaseous products from rapid thermolysis of TATB have been determined[198] and are discussed in section VI. Furazans and furoxans are detected in some thermal decomposition studies of TATB,[162,192-194] but not others.[195] These compounds are not likely to have a high steady-state concentration because they are less thermally stable than TATB. The gaseous products of decomposition of furoxans closely resemble those of TATB.[205]

A completely different view of thermal decomposition of TATB has been presented from MS studies by Farber and Srivastava.[196] The EI mass spectrum of the products following use of an effusion cell and Langmuir evaporation at 200–300 °C showed sublimation followed by splitting of TATB into two fragments of $m/e$ = 114 and 144. These two masses are consistent with fission of the molecular along the dashed line of VIII. Species having other $m/e$ values are detected as well that would result from various entities cleaved directly from TATB. These results are unique and perhaps reflect the conditions of the experiment more than the relevance to the behavior of TATB as a bulk explosive. For instance, they contradict the primary deuterium isotope effect found during decomposition of bulk TATB.[191] The value of $E_a$ = 43 kcal/mol in Table X from the MS studies[196] was determined from the rate of growth of $m/e$ = 114. This value of $E_a$ is disquietingly similar to $\Delta H_{vap}$ of TATB of 40 kcal/mol. Moreover, Langmuir evaporation and effusion cell results for another molecule, HMX, sharply differ from those of another MS technique, simultaneous thermogravimetry-modulated beam mass spectrometry.[38]



VIII

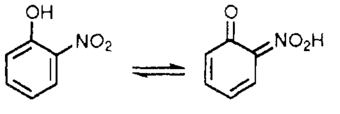
### 3. α-OH Bonds

The –OH group plays a major role in the thermal stability of nitroaromatic compounds, but the effect has to do with the tendency of –OH to become a quinoid

**Table XI. Arrhenius Data for Hydroxyl-Substituted Trinitrobenzene Compounds**

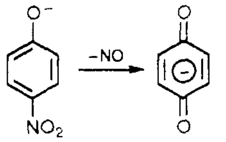
| compound | $T$, °C | $E_a$, kcal/mol | $A$, $s^{-1}$ | method | ref |
|---|---|---|---|---|---|
| PA | 183–270 | 38.6 | $10^{11.7}$ | EG | 210 |
| | 233–244 | 51.9 | | DTA | 56 |
| | 267–350 | 27.4 | | TTX | 94 |
| 1,3-$(OH)_2$-2-4,6-TNB | 180–200 | 34.6 | $10^{11.2}$ | EG | 210 |
| 1,3,5-$(OH)_3$-2,4,6-TNB | 145–165 | 54.3 | $10^{22}$ | EG | 50 |

group, rather than with cyclization. The $-OH$ group is a resonance electron donor as is the $-NH_2$ group. However, the $-OH$ substituent shortens the $C-NO_2$ bond and lengthens the N–O bond less than does $-NH_2$.[185,206] Since $-NH_2$ stabilizes the nitrobenzene backbone toward initiation by impact (Table I), it might be expected that $-OH$ also stabilizes the molecule compared to TNB. The opposite is found in practice because $-OH$ derivatives are more impact sensitive than TNB.[24] This has recently been explained computationally by the fact that the *aci*-nitro structure X has an energy minimum, but only 1.54 kcal/mol above IX.[185]



IX X

Upon shock or impact stimulus, vibrational excitation is proposed to place a significant fraction of the molecules into the more reactive form X.[185] This computational finding is consistent with a century of observations in organic chemistry. Quinones are isolated upon thermal decomposition of *p*-nitrophenols, eq 31.[207,208] The anionic quinoid form of X has long been suspected to be the source of bright color when picric acid (PA) dissolves in basic solution For this reason, nitrophenol compounds are useful pH indicators.

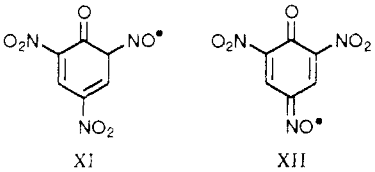


(31)

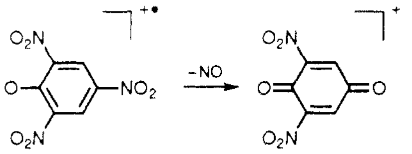
PA is an historically important explosive, but is hazardous because of its high shock sensitivity. The acidity of PA ($k_a$ = 1.6 × $10^{-1}$ M) is also detracting because it corrodes metal and attacks many organic materials. The resulting metal salts are quite sensitive to friction and impact. Despite these problems, PA was used extensively as an explosive up to World War II.

Compared to the $-CH_3$ and $-NH_2$ groups, relatively less work has been conducted on the details of thermal decomposition of hydroxyl-substituted nitrobenzene compounds.[209a,b] The behavior of PA is reminiscent of TNT and other nitroaromatics in that melting followed by decomposition occurs. The process is first-order autocatalytic after the initial induction period.[209a] Like TNT, the rate of decomposition in the gas phase is slower than in the liquid state suggesting that catalysis and intermolecular interactions are important. Arrhenius data are sparse, but are compiled in Table XI. The large variation in values makes conclusions difficult to draw. However, the TTX value[94] probably can be discarded because of the difficulty of obtaining efficient heat transfer.

The initial reaction step of PA at the temperatures in Table XI appears to involve the quinoid structure X on the basis of ESR,[211a] XPS,[209b] and MS studies.[126,132,170] There is no evidence of the quinoid form in the ground state.[211b] Radicals XI and XII that are readily formed from the equivalent of X were suggested to explain the ESR spectra of thermally decomposing PA.[211a] Structure XII and the isomer in which the nitroso group is *ortho* to the quinoid oxygen atom were suggested from XPS data.[209b] A thermal decomposition reaction that appears to be unique to PA (and MATB) is inferred from the ions in CI-MS[170] and MS/MS-CID.[126,132] This is loss of NO as the dominant decomposition pathway. In a manner similar to eq 31, resonance stabilization through the quinoid structure according to eq 32 was proposed to be the main reason for the faciléness of this process.



XI XII

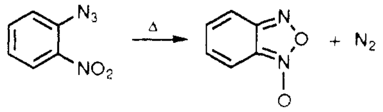


(32)

When all data are taken together, a clear understanding of the decomposition mechanism of PA does not exist. The mobility of the H atom bound to oxygen almost certainly plays a major role in thermal decomposition mechanism at lower temperatures. Unlike when $-CH_3$ and $-NH_2$ groups are *ortho* to $-NO_2$, cyclization does not occur. It is logical to extrapolate from the more extensive data available on $-CH_3$- and $-NH_2$-substituted trinitrobenzene compounds that $C-NO_2$ homolysis is also a major, if not the dominating, early reaction during impact and shock initiation of PA.

### *4. $-N_3$ Ortho to $-NO_2$*

The azide group cyclizes an *ortho* $-NO_2$ group in a manner resembling the behavior when $-CH_3$ and $-NH_2$ groups are *ortho* to $-NO_2$. Upon heating above 70 °C, 2-nitrophenyl azide eliminates $N_2$ and forms benzofuroxan according to eq 33. This reaction has been used for years as a facile synthetic route to substituted benzofuroxanes.[141,190,212] In the EI mass spectrum of 2-nitrophenyl azide, an $m/e$ = 136 fragment is observed corresponding to benzofuroxan.[64] Equation 33 contrasts with the behavior of *meta* and *para* isomers where

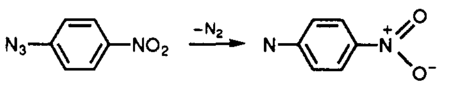


(33)

**Table XII. Arrhenius Data for Thermal Decomposition of Nitroazidobenzene Compounds**

| compound | $E_a$, kcal/mol | $A$, $s^{-1}$ | ref |
|---|---|---|---|
| 1,2-nitroazidobenzene | 26.1 | $10^{12.3}$ | 214 |
| 1,4-nitroazidobenzene | 40.6 | $10^{16.8}$ | 213 |
| 1,3,5-triazido-2,4,6-trinitrobenzene | 26.0 | $10^{12.1}$ | 106 |

the rate of thermolysis is $10^4$ times slower at 100 °C owing to a different decomposition mechanism, eq 34.[106,213]



(34)

The Arrhenius data compiled in Table XII reflect the significantly different rates of eqs 33 and 34. When *ortho* related $-N_3$ and $-NO_2$ groups are present on the ring, the decomposition rate is insensitive to the presence of other $-N_3$ or $-NO_2$ groups, because eq 33 dominates the process.[106] On the other hand, eq 34 is accelerated by the presence of electron-withdrawing groups *para* to $-N_3$.[215]

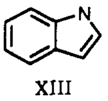
Whether eq 33 or eq 34 dominates has a pronounced effect on the burn rate of these compounds. Despite the higher $E_a$ of eq 34, the burn rates of 1,3- and 1,4-nitrophenyl azide are 1.4–1.7 times higher than 1,2-nitrophenyl azide.[106] This is because the nitrene product of eq 34 decomposes much more exothermically than the furoxan product of eq 33. Release of a large amount of heat early in the decomposition reaction scheme near the burning surface produces a high burn rate for the material.[216,217]

The initial decomposition chemistry when an azide group is present on a nitroaromatic backbone appears to be straightforward on the basis of the current knowledge of these compounds. However, the explosive characteristics of these compounds are essentially unknown.

### *5. Other Ortho Substituents*

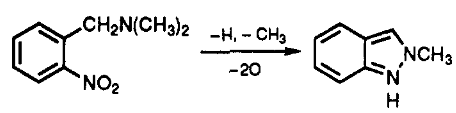
Cyclization of an $-NO_2$ group with an *ortho* substituent is so widely occurring that a few additional studies are worthy of mention to dispel any lingering thought that the results in sections IV.D.1, 2, and 4 are unique.

As noted in section IV.D.1, α-CH abstraction from a $-CR_2'R''$ group ($R' = R'' = H$; $R' = H$, $R'' = CH_3$; $R' = CH_3$, $R'' = H$) is a general reaction in the presence of an *ortho* $-NO_2$ group. However, further reaction of the molecule following this initial C–H abstraction step proceeds by different routes.[37] For instance, the formation of anthranil by eq 26 occurs for the $-CH_3$ group. On the other hand, (2-nitroethyl)benzene yields indole (XIII) through a series of H rearrangements.[37]



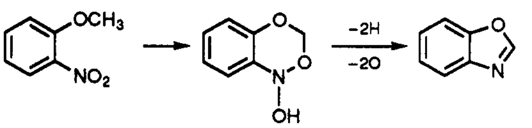
XIII

When $R' = H$ and $R'' = N(CH_3)_2$ eq 35 occurs in the sample on sitting at room temperature for several days.[218]



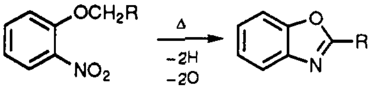
(35)

Unimolecular decomposition of 2-nitroanisole has been proposed to occur via H migration and ring closure, eq 36.[144] This species then collapses to benzoxazole.[37]



(36)

Such a rearrangement is consistent with the formation of a substituted benzoxazole when a longer alkoxy chain is present, eq 37.[219] Likewise, 2-nitro(methylamino)benzene was observed to form benzimidazole at a relatively low temperature by eq 38.[37] Benzofurazan is isolated from methyl $N$-(2-nitroaryl)carbamate according to eq 39.[220,221] Even 1,2-dinitrobenzene loses $O_2$ upon heating giving small amounts of benzofurazan and benzofuroxan[102,110] by eq 40.



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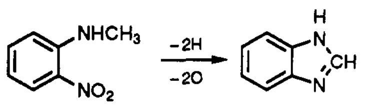

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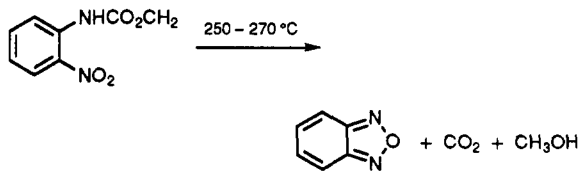

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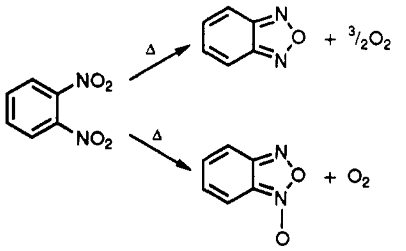


(40)

## *V. Effect of Substituents on the Kinetics of Thermolysis*

Throughout section IV, the positioning of a reactive substituent *ortho* to the $-NO_2$ group stands out as a very important factor in the low $E_a$ thermal decomposition pathways of nitroaromatic compounds. In this section a broader view is taken of the effect of various substituents on the decomposition rate.

Hammett championed the notion that rate constants of various reactions are related to the structure and composition of the parent aromatic molecule.[222,223] More specifically, the electron density of the aromatic ring influences the reactivity as mediated by the attached substituents. Linear free-energy relationships for the substituents were determined and are frequently referred to as Hammett or Taft constants.[224–226a] Recently, correlations of $\nu_s(-NO_2)$ obtained from Raman spectroscopy have been claimed to exist with substituent electronic effects.[226b] A small number of substituents were considered. Correlations fail when a larger number of substituents are used.[123]

An outstandingly prominent feature of polynitroaromatic compounds is that thermal decomposition data generally do not correlate with Taft or Hammett constants. The absence of correlation is independent of the phase of decomposition in that neither the gas phase nor the condensed phase kinetic data correlate.[52] Several possible reasons for noncorrelation exist. Hammett constants depend on the solvent and the temperature of measurement. First, the temperature at which polynitroaromatic compounds decompose is usually very different from the temperature at which the Hammett constants are determined. Second, the molecular environment during thermal decomposition is different from that in which the Hammett constants are determined. Third, the foregoing sections illustrate that catalysis and bimolecular processes frequently dominate during thermal decomposition of nitroaromatic compounds. Fourth, the rates of thermal decomposition of nitroaromatic compounds may not depend very much on the resonance and inductive electronic effects of the substituents. For example, $E_a$ values for thermal decomposition of nitrobenzene compared to various 1,3- and 1,4-substituted nitrobenzene compounds differ by only ±2 kcal/mol and the $A$ values differ by only a factor of 5.[52]

Despite the absence of correlations with Hammett constants, the substituents on the ring do have a profound effect on the explosive properties and the kinetics of decomposition. The most ambitious attempt to discover structure/reactivity/detonation relationships has been the work of Zeman *et al.*[5-8,54] That a relation might even exist could be traced to comments of Cook *et al.*,[3,4] who proposed that the early decomposition kinetics affect the detonation velocity of an explosive. Zeman *et al.* based their conclusions on values $E_a$ before the onset of autocatalysis; $T_D$, the temperature immediately after the onset of the exotherm; $P$, the C–J pressure; $D$, the detonation velocity; and $Q$, the heat of explosion. Equation 41 was used.

$$\log(E/T_D) = b(P/\rho, D^2, Q) + a \qquad (41)$$

The values of the constants $a$ and $b$ depend on the variable $P$, $D^2$, or $Q$ chosen. By using data for 74 compounds, 41 of which are nitroaromatic compounds without other energetic substituents, Zeman found groupings of 3–5 compounds that gave reasonably linear solutions of eq 41. One group contained 10 compounds. On this basis structure and electronic relationships were proposed to exist between the early kinetics of slow thermal decomposition and detonation.[6,7] Few of these groupings, however, are chemically satisfying. For example, the largest group containing 10 compounds contains both sensitizing (–OH) and desensitizing ($-NH_2$) substituents.[7] Another contains both $-CH_3$ and –Cl substituents,[5] which do not decompose by the same mechanism. In fact, Rogers *et al.*[191] would dispute the foundation of Zeman's assumed connection, at least for TATB. Zeman[5] also related the equilibrium constant for the activated complex, $K^{\ddagger}$, to $D$ on a log–log plot and found selected groupings of compounds in the 74 compound data base. A caveat is that a log–log plot tends to be relatively insensitive to curvature. Moreover, some of the correlations are rather loose, which partly reflects the difficulty of obtaining accurate experimental data. Zeman's DTA data are sensitive to the sample weight.[55,56,97-101]

As discussed in section II.D, interpretation of the explosive characteristics of aminonitrobenzene compounds in terms of ground-state molecular and electronic features in a risky adventure. Still the fact remains that the decomposition and explosive properties of nitroaromatic compounds are clearly sensitive to the substituents. Most relationships simply defy easy chemical interpretation. The trends in the liquid phase and the gas phase are usually different because of the role of catalysis, bimolecular processes, and the environment.

The remainder of this section illustrates several systematic attempts to determine the effect of the substituent on the decomposition rate.

According to the Hammett and Taft constants, the $-NO_2$ substituent is one of the strongest electron-withdrawing groups available. As a result, the ionization potential of the $\pi$-HOMO of the benzene ring increases as the number of $-NO_2$ groups increases.[227] Perhaps for this reason, the decomposition rate is faster as the number of $-NO_2$ groups on the ring is increased.[55,228] The relative rate constants at 330 °C in the gas phase[53] for $C_6H_5NO_2/1,3\text{-}(NO_2)_2C_6H_4/1,3,5\text{-}(NO_2)_3C_6H_3$ are 1:20:34. This is also the trend in the burn rate of these compounds at a given pressure and value of the pressure exponent.[106,229] The position of the $-NO_2$ groups relative to one another on the ring affects the reaction rate at 330 °C. This is evident for 1,2,3-TNB, 1,2,4-TNB, and 1,3,5-TNB which have relative decomposition rates of 1:0.175:0.03.[53] This trend suggests that within a given stoichiometry the thermal stability is improved by making the molecule more symmetrical.[230] Bliss *et al.*[181] explained this same pattern in the sensitivity to impact in terms of the greater ease of nitro–nitrite isomerization when $-NO_2$ groups are *ortho* related.

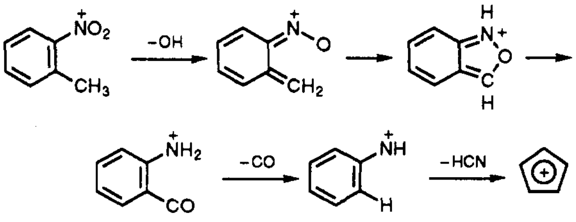
As substituents other than $-NO_2$ are added to the ring, resonance and inductive effects shift the $\pi$-MO's relative to one another in complex ways. The resulting effect on the rates of thermal decomposition frequently seems random. For example, –OH is thermally destabilizing. The addition of –OH increases the decomposition rate in the order:[228,230] 2,4,6-trinitrofloroglucinol > 2,4,6-trinitroresorsinol > 2,4,6-trinitrophenol > 1,3,5-TNB. This additivity effect is satisfying. On the other hand, the trend for multiple $-CH_3$ groups in the melt phase is reported not to be additive.[230] One $-CH_3$ group destabilizes the molecule while two and three $-CH_3$ groups stabilize it relative to TNB; *e.g.* the trend in thermal stability is TNT < 1,3,5-TNB < 2,4,6-trinitroxylene < 2,4,6-trinitromesitylene.[230] On the other hand, Oxley *et al.*[229] found that decomposition at 340 °C of 1.2 wt % of compound dissolved in $C_6H_6$ occurred in the reverse order of rates, *i.e.*, 2,4,6-trinitromesitylene was the fastest and TNT was the slowest. They attributed the increased stability in the condensed phase of compounds containing $-CH_3$ compounds to the increase in melting point and not to the intrinsic stability of the molecule. Other evidence exists that the kinetics of decomposition when the $-CH_3$ group is present is not trivially additive. Specifically, 2-NT is less thermally stable in the gas phase than nitrobenzene because of anthranil formation[33] (section IV.D.1), while 4-NT is more stable than nitrobenzene because of the lower *A* factor.[32]

A –Cl substituent destabilizes 2,4,6-trinitrochlorobenzene as revealed by the increase of a factor of 1.75 in the gas-phase reaction rate compared to 1,3,5-TNB.[53] When a second or third –Cl substituent is added to the TNB backbone, there is no further effect on the rate of decomposition.[53] In the condensed phase, one, two, or three –Br substituents on 1,3,5-TNB decreases the rate of decomposition, perhaps because of the increasing melting point.[229] Substituents with built-in reactivity[231] can override all of the conventional notions about thermal stability of the nitroaromatic ring. Furthermore, except for the "ortho effects" discussed in section IV, the MS cracking patterns of substituted trinitrobenzene compounds follow few systematic patterns.[126,170]

## VI. Later Stage Reactions

All of the forementioned thermolysis reactions of polynitrobenzene explosives have occurred among the substituents while leaving the aromatic backbone intact. These substituent homolysis and cyclization reactions are obviously early reactions of nitroaromatic explosives and can be thought of as initial steps in which little energy is generated. The next stage of thermal decomposition involves propagation reactions. These reactions involve exothermic oxidation and reduction that lead to lower molecular weight and thermodynamically stable gaseous products. While much is known about the related kinetics and thermochemistry of hydrocarbon/air flames[232–234] and nitrogen chemistry in combustion,[235] the processes by which large, energetic molecules thermolyze in the bulk phase to form the reactants for the high-temperature flame or detonation wave is a challenging area of research.[41,107,217] Specifically, what are the intervening steps when 2,4-DNAn or the dinitrotoluene radical proceed to CO, NO, $CO_2$, HCN, $N_2$, and $H_2O$?

At least in the gas phase according to MS/MS/CID,[134] ring dissociation does not occur until most of the attached substituents have been removed. On the other hand, dissociation of $NO_2$ from the ring is proposed to leave the aromatic radical with excess internal energy to engage in further reactions.[111] In the simplest situation, the EI mass spectrum gives a scheme for further unimolecular reactions of the aromatic ring in the collisionless gas phase. 2-Nitrotoluene is believed to react further according to eq 42 on the basis of $^2H$ and $^{13}C$ labeling.[36] Consistent with this scheme is the fact that anthranil (eq 12) decomposes by rupture of the NO bond with a rate constant[34] of $k = 3.7 \times 10^{15}$ exp($-51084/T$) $s^{-1}$. The large *A* factor is in line with high entropy of the transition state. The proposed pathway for anthranil degradation is eq 43.[34]



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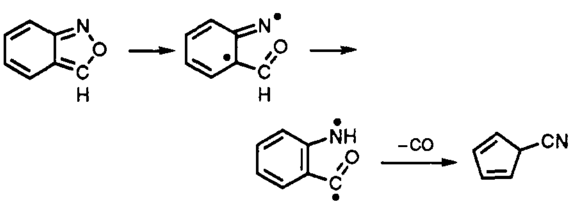

(43)

The relevance of the findings described above to neutral molecules in the bulk state of an explosive is dubious. Bimolecular processes and the competition of radical and ionic pathways is not considered. In fact, attack on the ring is quite plausible because the aromaticity of the benzene ring is reduced by ring closure to anthranil (eq 12), or furazan/furoxan species (eq 14). This makes the ring more susceptible to reactions that ultimately lead to C–C bond cleavage. For example, trinitroaromatics are notoriously susceptable to nucleophilic addition[236–238] which also reduces the aromaticity. While $NO_2(g)$ is not liberated to any great extent from decomposition of trinitroaromatic explosives at temperatures below about 700 °C, $NO_2$ or NO from thermal decomposition in the bulk phase may be attacking the aromatic ring producing CO and $CO_2$. Maksimov[63] examined the decomposition of TNB vapor and noticed first a rise and then a drop in the NO concentration, which was attributed to the reaction of a nitrosoaromatic compound, RNO, with NO according to eq 44. The NO consumption occurs as $CO_2$ is formed,

$$RNO + 2NO \rightarrow R^{\bullet} + N_2 + NO_3^{\bullet} \qquad (44)$$

perhaps owing to the reaction of the nitrate radical with $R^{\bullet}$.[63]

The energy released by the propagations reactions of polynitroaromatic explosives is sometimes reflected in the relative concentrations of the gaseous products that are liberated after the exotherm. These reactions may have a role in the sensitivity, in addition to their important role in the performance of the explosive.[198] As an example, Table XIII gives the relative percentages of the IR-active products from TNB, MATB, DATB, and TATB at 520 °C.[198] Products having endothermic heats of formation (NO, HCN, and $N_2O$) appear when $-NH_2$ groups are present on the ring. HNCO also increases as the $NH_2$ content increases. Even though the C/O ratio in this series of parent compounds remained fixed, the $CO_2$/CO ratio increases as the $NH_2$ content increases. The energy distribution among the gaseous products reflects the fact that the heat of explosion of TNB is higher than those of the aminonitrobenzene explosives (Table I). The high heat of explosion of TNB results from the dominance of products with negative $\Delta H_f°$ (CO, $CO_2$, HNCO) and the absence of products with positive $\Delta H_f°$ (NO, HCN, $N_2O$). For MATB, DATB, and TATB the amount of energy from the exothermic product (CO, $CO_2$) is lower than for TNB and is further aggravated by the formation of endothermic products (NO, HCN, $N_2O$). In sum, the energy output of TNB results from a different set of propagation reactions than occurs for MATB, DATB, and TATB.

## VII. Conclusions

Despite much careful research on thermal decomposition of nitroaromatic explosives, large voids of

**Table XIII. Quantified Gas Products from Heating at 2000 °C/s to 520 °C under 10–40 atm Ar**

| | percentage | | | | | |
|---|---|---|---|---|---|---|
| compound | $CO_2$ | CO | NO | HCN | $N_2O$ | HNCO |
| TNB | 6 | 94 | | | | |
| MATB | 17 | 38 | 28 | 13 | | 3 |
| DATB | 20 | 31 | 21 | 18 | 2 | 8 |
| TATB | 27 | 20 | 26 | 13 | 3 | 11 |

knowledge exist in several crucial areas. Among the foremost problems are as follows:

(a) The rates and mechanisms of specific reactions in the neat, bulk compound are extremely difficult to determine and remain essentially unknown.

(b) The balance between ionic and radical reaction pathways in the bulk material undoubtedly depends on the conditions and is poorly understood.

(c) Almost all studies employ only temperature as the intensive variable. The role of pressure on the rates and mechanisms of reactions of nitroaromatic explosives is essentially unknown.

(d) In terms of specific reactions, knowledge about aromatic $-NO_2$ to $-ONO$ isomerization is the most deficient, especially in the condensed phase.

A relatively fruitless approach to understanding the shock and impact sensitivity of nitroaromatic explosives is the comparison of these properties to the parent ground-state molecular and electronic structure. The parameters that control shock and impact sensitivity in this type of compound only partially depend on the molecular and electronic structure of the compound. Physical properties, such as the void volume and density, are very important. An essential point of this review is that the rates and types of chemical reactions are equally important.

From the analysis presented it is understandable why the time-to-explosion does not correlate with the molecular and electronic characteristics, such as are reflected in the Hammett or Taft linear free-energy relationships. The time-to-explosion at times longer than about 0.1 s is controlled by catalysis of the decomposition products of the parent molecule and not the parent molecule *per se*.

In general, the thermal decomposition of nitroaromatic explosives begins with one or more endothermic initiation steps. These steps include $C-NO_2$ homolysis, isomerization of the nitro group to the nitrite linkage, and reactions of the nonenergetic substituent on the ring. The relative importance of these initiation steps depends on the temperature and pressure reached during stimulus. To the extent that the rate data can be trusted, shock initiation predominantly causes $C-NO_2$ homolysis in TNT and the aminonitrobenzene series. Impact initiation results in competitive contributions of $C-NO_2$ homolysis and reactions involving the nonenergetic substituent, especially in the case of TNT. Decomposition at lower temperature favors reactions of the nonenergetic substituent, whereas higher temperature favors homolysis of the bonds.

Following the initiation reaction steps, the gas/solid products differ depending on the temperature. The propagation steps that follow will therefore differ. In turn, the explosive characteristics differ from compound to compound. For example, as the number of $-NH_2$ groups increases in the aminonitrobenzene series, the quantity of products with positive heats of formation increases relative to the products with negative heats of formation. This difference causes a decrease in the heat of explosion as $-NH_2$ groups are added to the ring and may even affect the view of sensitivity.

*Acknowledgments.* The financial support of the Wright Laboratory, Armament Directorate, Eglin AFB, FL, is gratefully acknowledged. Dr. Robert L. McKenney, Jr., was the program manager.

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