UCRL-CONF-209023

A Detailed Chemical Kinetic Model for TNT

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January 14, 2005

2005 Joint Meeting of the U.S. Sections of The Combustion Institute
Philadelphia, PA, United States
March 20, 2005 through March 23, 2005

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Abstract

A detailed chemical kinetic mechanism for 2,4,6-tri-nitrotoluene (TNT) has been developed to explore problems of explosive performance and soot formation during the destruction of munitions. The TNT mechanism treats only gas-phase reactions. Reactions for the decomposition of TNT and for the consumption of intermediate products formed from TNT are assembled based on information from the literature and on current understanding of aromatic chemistry. Thermodynamic properties of intermediate and radical species are estimated by group additivity. Reaction paths are developed based on similar paths for aromatic hydrocarbons. Reaction-rate constant expressions are estimated from the literature and from analogous reactions where the rate constants are available. The detailed reaction mechanism for TNT is added to existing reaction mechanisms for RDX and for hydrocarbons. Computed results show the effect of oxygen concentration on the amount of soot precursors that are formed in the combustion of RDX and TNT mixtures in N_2/O_2 mixtures.

Introduction

Destruction of outdated munitions is conventionally carried out by combustion, either via enclosed incineration, or by open burning or detonation. Soot emissions during this destructive combustion have become a serious problem for environmental reasons. There is also a continuing need from both civilian and military users of explosives to improve explosives performance and safety against accidental initiation. Just as in the case of combustion systems using conventional hydrocarbon fuels, the opportunity to use kinetic modeling can provide valuable tools to assist in solving these problems.

Major obstacles exist for developing kinetic mechanisms for explosives. First, most such explosives include more types of atoms than are present in familiar hydrocarbons, with which kinetic modeling is most experienced. In particular, many explosives include N atoms in the form of nitro and amino groups, as well as N atoms substituted for C atoms in ring structures. Figure 1 shows some important explosives molecules and illustrates the considerable presence of N atoms.

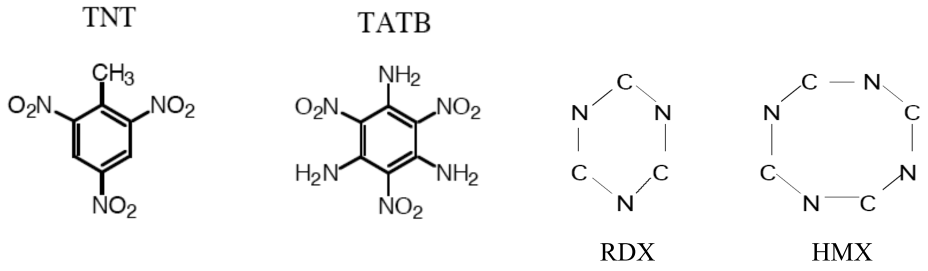

Figure 1. Four common high explosives molecules in common use. Two additional H atoms (not shown) complete the aromatic ring for TNT. Each C in RDX and HMX has two additional H atoms not shown, and each N shown in RDX and HMX has an additional NO_2 group not shown here.

These are large molecules, often based on aromatic hydrocarbon backbones, and the current frontier of kinetic combustion modeling is at this same level of simple aromatic hydrocarbons like benzene and toluene. Reaction mechanisms for these species are necessarily as large and complex as any currently being developed in conventional energy applications. The extreme energy content of these explosives molecules means that they react so rapidly and violently that careful laboratory experiments are extremely difficult or impossible, so the available experimental database is very small for comparisons with computed results. In the first generation of model results, sensible qualitative predictions are probably all that can be expected, but we have found that such qualitative and semi-quantitative results are very useful. Finally, all of the high explosives shown above are solids at room temperature and pressure, making their atmospheric combustion a multiphase technical problem. Such problems are also at the frontier of combustion simulations [1].

Kinetic Model Development

Previous high explosive kinetic reaction mechanisms have been developed for only a few gas phase and condensed phase explosives. Tieszen et al. [2] developed kinetic models for hexyl nitrate and nitroethane and used them to predict ignition and detonation cell sizes for use as a fuel/air explosive (FAE**).** Melius [3] developed the first mechanism for any of the compounds in Fig. 1 building on a relatively simple hydrocarbon mechanism by adding reactions of RDX itself and the subsequent decompositions of the radical products of RDX and used it to model the RDX flame of Ermolin et al. [4].

Prasad, Yetter and Smooke [5] further developed the kinetic model for RDX, modeling both the liquid phase and the gas phase kinetics. The resulting mechanism included 3 reactions in the liquid phase and 48 chemical species and 228 elementary reactions in the gas phase. They used their model to simulate the flame structure of a laser-supported deflagration of an RDX flame [6]. The present modeling project was motivated by two factors, both of which led to the selection of TNT as a model high explosive fuel. Unlike RDX, TNT is based on an aromatic ring and resembles the purely hydrocarbon toluene, which has been the subject of our recent kinetic modeling attention [7] and thereby provides a core reaction mechanism on which to build a TNT model. In addition, while both RDX and TNT are important explosives in real applications, some particularly important practical explosives consist of mixtures of RDX and TNT; CompB3 is made of 40% TNT and 60% RDX, so the availability of a TNT reaction mechanism would make it also possible to simulate CompB3 kinetics as well as TNT and RDX individually. Therefore, the present TNT kinetic reaction mechanism has been built on our existing toluene mechanism [7] and the RDX mechanism of Prasad et al. [5]. Addition of TNT eventually resulted in inclusion of 30 new chemical species and 47 new elementary reactions.

Thermochemical parameters for the new species were estimated using principles of group additivity, using the THERM code of Ritter and Bozzelli [8,9] to calculate heats and enthalpy of formation, as well as temperature-dependent specific heats. Some groups were corrected to reflect heat of formation values in the literature. For example, the heat of formation for the CB/NO_2 group was corrected by 4.4 kcal/mole so that the group additivity estimate would give the heat of formation for nitrobenzene (16.38 kcal/mole) in the NIST database [10]. The NIST value agrees with the calculated BAC/MP4 value (14.18 kcal/mole) of Melius [11] after correcting a 2 kcal/mole BAC/MP4 systematic error for the benzene ring. However, for a considerable fraction of the 30 new species required, no previous thermochemical data were available. A representative sample of this data is summarized in Table I.

SPECIES	Hf	S	Cp 300	400	500	600	800	1000	1500
TNT	1.55	112.64	52.12	62.40	70.74	77.52	87.81	94.75	104.70
TNBENZYL	38.45	110.08	52.87	63.00	70.87	77.10	86.40	92.57	101.33
TNTJ	62.45	114.12	51.71	61.22	68.81	74.83	84.06	90.27	99.46
DNT	4.97	101.15	43.10	52.66	60.62	67.16	77.10	83.92	93.87
DNTJ	65.87	102.63	42.69	51.48	58.69	64.47	73.35	79.44	88.63
NT	8.39	89.67	34.08	42.92	50.50	56.80	66.39	73.09	83.04
NT-2	8.39	89.67	34.08	42.92	50.50	56.80	66.39	73.09	83.04
DNTOH	-37.13	108.52	48.06	58.02	66.18	72.69	82.48	89.02	98.65
DNT-OJ	-2.73	109.82	46.48	55.78	63.51	69.76	79.27	85.61	94.84
TNPH	9.54	100.07	46.50	55.86	63.12	68.88	77.37	82.95	90.87
TNPHJ	70.44	103.73	46.09	54.68	61.19	66.19	73.62	78.47	85.63
MEDNCP	9.68	69.56	30.83	40.79	49.26	55.19	64.40	70.29	79.37
MEDNCPDJ	35.58	70.84	31.12	40.79	48.69	54.01	62.14	67.20	75.03
TNPHC*O	-19.16	117.70	54.30	64.16	71.86	78.00	87.25	93.05	.00
TNPHCJ*O	15.74	116.31	54.11	63.31	70.27	75.79	84.04	89.16	.00
TNPHOH	-32.56	109.62	51.46	61.22	68.68	74.41	82.75	88.05	95.65
TNPHOJ	1.84	110.92	49.88	58.98	66.01	71.48	79.54	84.64	91.84
C#CC*CNO2	35.45	77.15	22.60	26.97	30.25	32.76	36.47	39.20	43.15
C#CC*CJN	94.55	78.54	22.41	26.22	28.89	30.84	33.65	35.71	38.62

Table I. Thermochemical data for some species included in TNT kinetic reaction mechanism. Hf=enthalpy of formation at 298K in kcal/mole, S=enthalpy at 298K in cal/mole-K, Cp = specific heat at constant pressure in cal/mole-K. (TNT = 2,4,6-tri-nitrotoluene, TNBENZYL = 2,4-6-tri-nitrobenzyl radical, TNTJ = 1-methyl-2,4,6-trinitrophenyl radical, DNT = 2,4-di-nitrotoluene, DNTJ = 1-methyl-4,6-di-nitrophenyl radical, NT = nitrotoluene, TN-2 = 2-nitrotoluene, DNTOH = 2-methyl-3,5-nitro-phenol, DNT-OJ = 2-methyl-3,5-nitro-phenoxy, TNPH = 1,3,5-tri-nitro-benzene, TNPHJ = 1,3,5-tri-nitro-phenyl, MEDNCP = 1,3-nitro-5-methyl-1,3-cyclopentadiene, MEDNCPDJ = 1,3-nitro-5-methyl-1,3-cyclopentadienyl radical, TNPHCJ*O = 2,4,6-tri-nitro-phenyl-formyl radical, TNPHOH = 2,4,6-tri-nitrophenol, TNPHOJ = 2,4,6-tri-nitrophenoxy, C#CC*CNO2 = 1-nitro-2-ethynyl-ethene, C#CC*CJN = 1-nitro-2-ethynyl-vin-1-yl)

In a very similar fashion, the rates of elementary reactions were estimated when possible on the basis of known reactions for related species, drawing heavily on the work of Brill and James [12]. For example, the principal initiation reaction for TNT involves breaking a C - N bond to produce NO_2. The rate constant used in the present model, k_{TNT}, was based on the measured rate constants of the analogous reaction of 2-nitro-toluene (2-NT) and 4-nitro-toluene (4-NT) measured by Tsang et al. in a shock tube [13]. Since TNT has two groups ortho to the methyl and one group para to the methyl, the rate constant was assume to be: $k_{TNT} = 2k_{2\text{-nt}} + k_{4\text{-nt}}$. This reaction was found to be the primary reaction consuming TNT in the simulations performed in this study. Additionally, reactions were added to the reaction mechanism for isomerization of the -NO_2 group to -ONO and for breaking a C-CH_3 bond. These reactions were minor contributors to TNT consumption under the conditions of this study. A similar example of a rate constant estimate is one of the subsequent reactions of the methyl-di-nitrophenyl radical (DNTJ) produced by the initiation step. An important reaction for the DNTJ radical is its reaction with NO_2 that leaves an O atom on the phenyl radical site and an NO product, as shown in Fig. 2.

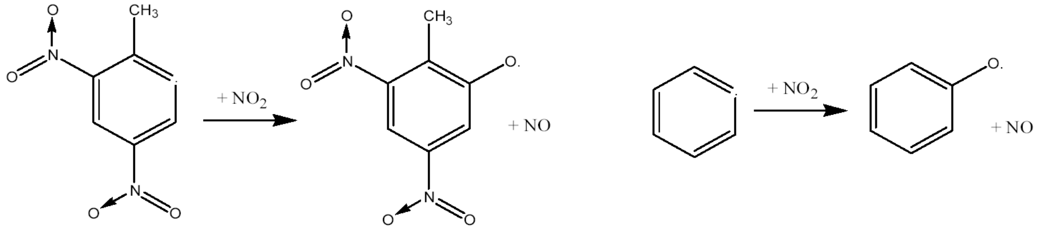

Figure 2. Reaction of dinitrobenzyl radical with NO_2 (left), and analogous reaction (right) of phenyl radical studied by Preidel and Zellner [13].

The analogous reaction of phenyl and NO_2 was studied by Preidel and Zellner [14], and this rate was used for the new reaction in the TNT mechanism. The reaction of DNTJ and NO_2 was the primary Rates of H atom abstraction reactions in TNT were estimated as equal to H atom abstractions by the same radical in toluene, again corrected for the relative numbers of available H atoms. Other reaction rates, particularly for radical decomposition reactions and for complex addition/decomposition reactions, were estimated based on the rates of the reverse addition reactions and the relevant equilibrium constants. Examples of selected reactions with their modified Arrhenius rate coefficients are shown in Table II.

	A	n	Ea (cal)
tnt+o2=tnbenzyl+ho2	9.30E+08	1.3	40939.0
tnt=dntj+no2	8.54E+14	0.0	61470.0
tnt=tnphj+ch3	7.94E+16	0.0	104000.0
tnt=dnt-ono	1.00E+13	0.0	55980.0
dnt-oj+no=dnt-ono	5.44E+13	-0.7	0.0
tnt=tnbenzyl+h	3.10E+15	0.0	89210.0
tnt+h=dnt+no2	7.57E+18	-1.7	6410.0
dnt+h=nt+no2	5.05E+18	-1.7	6410.0
nt+h=c6h5ch3+no2	2.52E+18	-1.7	6410.0
tnt+h=tnph+ch3	7.57E+18	-1.7	6410.0
tnt+oh=tnbenzyl+h2o	5.19E+09	1.0	874.0
tnt+h=tnbenzyl+h2	4.00E+02	3.4	3120.0
tnt+ch3=tnbenzyl+ch4	2.21E+00	3.5	5675.0
tnt+o=tnbenzyl+oh	6.00E+10	0.7	7632.0
tnt+ho2=tnbenzyl+h2o2	1.02E+04	2.5	12340.0
tnt+no2=tnbenzyl+hono	1.20E+13	0.0	30000.0
tnt+h=dntj+hono	3.18E+15	0.0	15700.0

Table II. Modified Arrhenius coefficients for selected reactions in TNT mechanism. Units are cal-mole-sec. (dnt-ono = 2-methyl-3,5-nitro-phenylnitrite. The other species are identified in Table I).

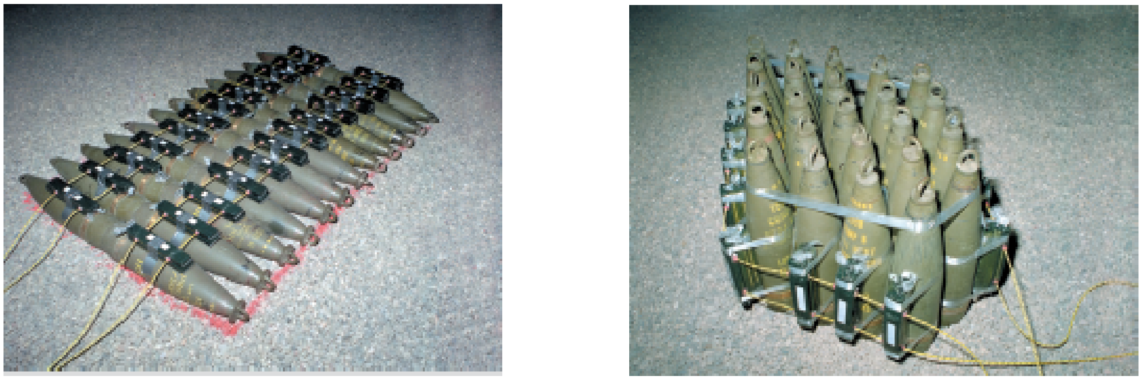

Figure 3

Model Applications

The specific application chosen to test the TNT reaction mechanism originated from the problem of open destruction of old munitions. In a typical case, a number of munitions, with their high explosive content included, are placed in an open pit in the ground and detonated almost simultaneously. Two typical arrays are shown in Figure 3. This is a very complex combustion problem if it were to be treated in its entirety, since the explosives are present in discrete units, and the cases and other peripheral materials are also involved in the overall explosion. However, in our simulation, we idealize or assume almost everything in this problem, with the exception of the detailed reactions of the explosive fuel.

We begin by assuming that all of the predictable combustion will occur in the gas phase. We also disregard all of the metal components including the munitions cases. We then treat the high explosives combustion as a homogeneous ignition problem. The explosive combustion is initiated by some sort of igniter that brings the explosive to a somewhat elevated temperature at atmospheric pressure. Once the explosive is ignited, it burns very rapidly, using the limited amount of oxygen already in the explosive molecule, together with oxidizer in any air which is assumed to be entrained into the reacting explosive material.

The amount of air entrainment is another quantity that is assumed for the ignition calculations. The overall amount of fuel converted to final products is limited by the amount of oxygen in the entrained air, and for the purposes of these munitions destruction calculations, the amount of available air is insufficient to convert everything to H_2O, CO_2 and N_2. In principle, the problem of explosive rupture of a single isolated shell, the reactive flow and entrainment of air into the reacting gases, and the eventual reaction quenching as the reactants and products expand could all be computed, but this would be a very ambitious 3D or possibly 2D axisymmetric calculation in which detailed chemical kinetics could probably not included. Instead, making these rather sweeping simplifications, it is possible to examine the chemical kinetic factors involved in the combustion and develop a general understanding of the chemical features of the problem. The limitations of this approach suggest that we not put too much faith in the details of the calculations and use the results only for general guidance.

The same overall assumptions have been used very productively in simulating diesel ignition [15] and then in understanding the role of added oxygen on soot formation in diesel engine combustion [15-18]. In those problems, just as in the present munitions simulations, the details of how the air is entrained into the fuel-rich reaction zone are not as important as the fact that air is entrained and not enough is entrained to consume all of the fuel. With these simple limitations, the evolution of the fuel-rich combustion leads to some very tangible and realistic chemical predictions.

Soot Production Chemistry

A considerable body of kinetic research has established that soot is produced by the growth of large polycyclic aromatic hydrocarbon species that grow by addition of small, usually unsaturated hydrocarbon fragments and molecules. Acetylene and hydrogen, together with vinyl and propargyl radicals are particularly effective growth species for soot growth. Many sooting fuels already have aromatic species present in the fuel itself, as is the case with conventional diesel and jet fuels, which greatly facilitates sooting with these fuels. If the fuel initially contains no aromatic hydrocarbons, the post-ignition fuel components have been shown to manufacture these aromatic soot seed molecules by a variety of kinetic processes in which acetylene molecules and propargyl and cyclopentadienyl radicals have been shown to be especially effective [19-21].

We have demonstrated [15] that ignition under diesel conditions takes place under very fuel-rich conditions, and that the products of this fuel-rich ignition then react to produce soot precursors and participate in soot growth kinetics. The addition of oxygen in the form of oxygenated diesel fuels [16-18] or excess air [22] changes the kinetics of this ignition environment and reduces the amount of soot produced. Kinetic modeling has shown that the extra oxygen reduces the post-ignition concentrations of those same hydrocarbon fragments that produce initial aromatic species and then participate in soot growth reactions.

Soot Production in TNT Combustion

Our simulations of TNT ignition and burning followed exactly the same logical pathway as for diesel ignition. We know that reaction ignition starts combustion of the explosives, and that the reacting fuel then entrains some amount of air. We assumed that the overall equivalence ratio in the reacting explosive mixture was approximately the same as that in the diesel engine at the time of ignition, although there is no direct basis for assuming it being either smaller or larger that in the diesel environment. One factor involved in making our estimates was the fact that large quantities of soot were really observed in the actual destruction experiments. As a result, we assumed as initial conditions an amount of air mixed with the gaseous TNT at an initial temperature of between 900K and 1400K, making an overall TNT-rich equivalence ratio of about 3.0. Of course, even at 100% TNT, there is still some oxygen in the TNT molecule, so the definition of an overall equivalence ratio is still a bit ambiguous.

The ignition of the TNT/air mixture was followed effectively to conclusion in each computation, and at the end of each computation, we calculated the sum of the concentrations of each species that we identified with soot production, including acetylene, benzene, ethylene, toluene, and propene. An example of the results of such a calculation is shown in Figure 4, showing the soot precursor level as a function of time with pure TNT and no air entrainment.

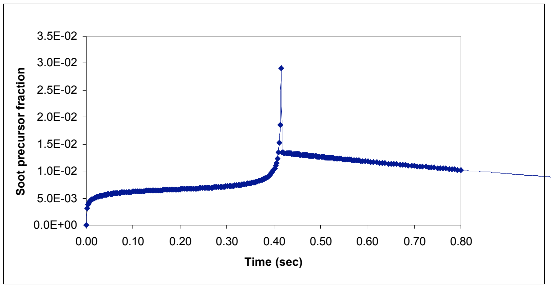

Figure 4. Time dependence of soot precursors during ignition of TNT, with no added oxygen. Ignition occurs at 0.4 seconds, residual soot precursors remain at extremely high level of about 1% following ignition.

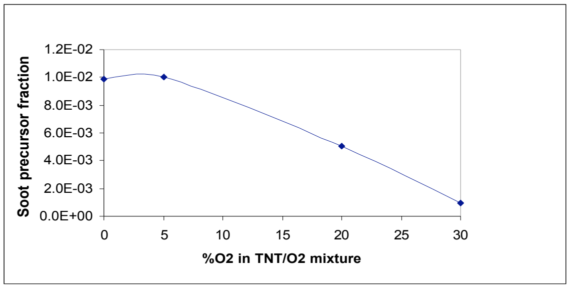

Figure 5. Computed variation in residual soot precursors with added oxygen in TNT ignition. Note that the value for no added oxygen is the residual, late time value shown in Figure 4.

As pure O_2 is added to the TNT and the ignition calculation is repeated, the level of post ignition soot precursors steadily declines, as shown in Figure 5. It is interesting to note that similar calculations under diesel conditions [16] as well as actual diesel engine experiments [23] both showed that soot and soot precursor production completely disappeared by the time the fuel consisted of 25 - 30% O_2, rather astonishingly similar to the results summarized for TNT ignition in Figure 5.

When the same calculations were repeated with RDX as the explosives fuel, the computed soot precursor concentrations were effectively zero, even without any O_2 addition to the RDX. This was found to be in good agreement with actual experimental observations that RDX is found to produce little or no soot when burned or detonated in the open atmosphere. An examination of the structure of RDX in Figure 1 shows that there are no C - C bonds in RDX, so the production of species such as acetylene, ethylene and any others with C - C single or double bonds would be expected to be very small. More detailed kinetic analysis of the results of the RDX calculations showed that a considerable fraction of the C atoms remain permanently bonded to N atoms, making them unable to participate in building aromatic or other soot precursor species.

Comparative analysis of the TNT molecule in Figure 1 shows that the fuel is already based on an aromatic structure, and there are nearly limitless possibilities for production of small fragment species with single, double and triple C - C bonds as soot precursors and growth species. The computed results showing large amounts of soot production in TNT combustion and virtually none in RDX combustion is completely consistent with experimental observations and operational experience, and the kinetic analysis traces these tendencies directly to the molecular structures of the two explosives molecules.

A final observation on the amount of oxygen required to eliminate soot production by TNT is that the 30% O_2 indicated in Figure 5 is a molar percentage, which can be converted to a 1:1 volumetric ratio if the oxygen is provided at 80 - 100 atm pressure, which is commonly available in pressurized laboratory gas containers. An array such as those in Fig. 3, with pressurized oxygen containers alternated with TNT munitions of similar overall size, might provide enough mixing between TNT and oxygen to significantly suppress soot production. This concept is awaiting experimental testing, although the required amounts of oxygen might be more conveniently or more economically provided in other ways than in the form of pressurized containers.

Conclusions

A detailed chemical kinetic reaction mechanism has been developed for TNT, based on existing models for toluene, nitrobenzene, and other related species. The mechanism was used to study soot production during open combustion of TNT munitions, and the model predicted soot precursor levels consistent with experimental observations. Comparable calculations for a different high explosive, RDX, showed that unlike TNT, RDX produced no soot or soot precursors, again in excellent agreement with experimental observations. This combination of computed results gives good credibility to the new TNT reaction mechanism, but many additional model tests are necessary to validate and improve the reaction mechanism.

Acknowledgments

The authors thank Dr. C. F. Melius for helpful discussions on the chemical kinetic mechanism. The work was supported by the Joint DoD/DOE Munitions Technology Program and performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No.W-7405-Eng-48. The authors thank Jim Wheeler, Director of the U. S. Army's Defense Ammunition Center, and Bruce Watkins, LLNL program manager, for their support of this work.

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