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14. ABSTRACT This report results from a contract tasking Centre National de la Recherche Scientifique as follows: The prospect of hypergolically igniting Ionic Liquids (ILs) requires a detailed understanding of the underlying chemical pathways and the reaction mechanisms involved when ILs are treated with NTO or any suitable oxidizer (RFNA, WFNA). The potential to develop hypergolic ignition as a suitable option for space propulsion applications requires gas-phase thermodynamic and chemical kinetic data. The contractor will investigate and accomplish the following: - A bibliography - An estimation of thermodynamic properties (gas-phase standard enthalpy of formation at 298.15 K, gas-phase standard Cp in the 300-5000 K range, gas-phase standard entropy in the 300-5000 K) of the reactants, products and intermediates needed to simulate the hypergolic ignition/combustion of ILs-based systems (to be defined), - Writing of the corresponding detailed chemical kinetic models (one for both ignition and combustion), - Calculation or estimation of rate constant if no experimental data are available,					
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CHEMICAL KINETICS INTERPRETATION OF HYPERGOLICITY OF IONIC LIQUID-BASED SYSTEMS

Writer	Supervisor
Laurent CATOIRE, Ph. D. Professor, University of Orleans, Chemistry Dept. and ICARE (Institute for Combustion, Aerothermic, Reactivity and Environment) CNRS (French National Center for Scientific Research)	Iskender Gökalp, Ph. D. Head of ICARE (Institute for Combustion, Aerothermic, Reactivity and Environment) CNRS (French National Center for Scientific Research)
	



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After two previous reports devoted to bibliographic study (interim report # 1) and thermodynamic calculations (interim report # 2), this final report examines the thermochemistry and reactivity of gaseous mixtures formed above ionic liquids (ILs) when mixed with white fuming nitric acid (WFNA). After a general introduction on the interesting results recently observed in this field by Chambreau and Vaghjiani et al. (2008) at the Air Force Research Laboratory (AFRL), Edwards AFB, this report will discuss the thermochemistry of imidazoles, triazoles, tetrazoles, and nitro compounds, which are energetic compounds for which relatively little thermodynamic data is available. Then, the reactivity of the gas phase above the reacting ILs-WFNA liquid mixtures will be examined by performing calculations at thermodynamic equilibrium as described in interim report # 2.

Lastly, a detailed chemical kinetics model will be proposed to tentatively explain the gas phase processes that lead to ignition in such systems. To our knowledge, this model represents the first ever attempt to predict hypergolic ignition delay times in ILs-WFNA mixtures. Our preliminary sensitivity analysis study of the model provides information on reaction steps that may be important in determining the ignition delay. Future efforts to refine the present reaction mechanism data set, together with incorporation of new experimental kinetics information as it becomes available, as well as inclusion of fluid dynamical effects will significantly enhance the fidelity of the model to quantitatively predict observed ignition delays in ILs-WFNA hypergol mixtures under typical laboratory conditions.

1. Introduction

The beginning of the 21st century is particularly interesting from an energetics point of view. On one hand, the increase in pollution and greenhouse effects can be correlated to the rapid increase in combustion of fossil fuels. On the other hand, serious depletions of known reservoirs and scarcity of easily extractable new fossil fuel sources has led to the search for new high-energy density and environmentally benign fuels. These new fuels are not totally “green” but they address, at least partially, some of the drawbacks of current fuels and combustibles. It is the case for gasoline and diesel that bio-ethanol and methyl esters of vegetable oils, respectively, will be the likely replacement candidates. This ecological concern is not limited to automobile fuels but extends to all fuels and combustibles, including space fuels, although, the quantities needed for space fuels are somewhat marginal compared to ground transportation fuels. One of the most utilized bipropellant combinations for propulsion of satellites and for interplanetary missions that fall under this scope is

monomethylhydrazine/nitrogen tetroxide (MMH/NTO). These propellants have the advantage of being earth-storable liquids (non-cryogenic); however, their vapors are highly toxic and carcinogenic, and their time-weighted average (TWA) exposure and threshold limit value (TLV) are rather low for these compounds. Moreover, because MMH has a positive enthalpy of formation, it is able to sustain a decomposition flame, and therefore can be hazardous even in the absence of an oxidizer. Furthermore, MMH compatibility is poor with many materials on which it can rapidly decompose exothermically upon contact. Similarly, NTO is corrosive to many materials. It is clear from the above facts that there are numerous valid arguments to search for suitable replacements for MMH. Finding a replacement for NTO is also of interest but probably less crucial. For instance, NTO could be replaced by nitric acid (or by any other suitable oxidant) when necessary. Among some of the alternative replacements proposed for MMH are ionic liquids which exhibit much lower vapor pressures than MMH, and have better TWA and TLV characteristics.

However, the main interesting feature of the MMH/NTO bipropellant combination is that MMH and NTO form mixtures that autoignite at room temperature and at low pressures. Understanding this autoignition or hypergolicity is therefore of major interest and a significant challenge in finding a suitable MMH replacement. Only in the last 15 years has there been much effort to fundamentally understand the hypergolic chemistry of MMH/NTO, even though the utility of this combination has been known since the 1950s. The first process in finding a suitable hypergol replacement has been in identifying fuels that are environmentally friendly, or at least easier to handle, store and transport. Certain ionic liquids have been shown to provide these advantages. The potential to develop hypergolic ILs as a suitable option for space propulsion applications requires the availability of comprehensive gas phase thermodynamics and chemical kinetics databases. The prospect of hypergolically igniting

these ILs also requires a detailed understanding of the underlying chemical pathways and the reaction mechanisms involved when ILs are treated with NTO or any other suitable oxidizers such as inhibited red fuming nitric acid (IRFNA) or white fuming nitric acid (WFNA). The literature in this regards is very sparse for ILs. Therefore the ignition chemistry and combustion chemistry of these ILs remain largely unknown as is their hypergolicity with NTO, IRFNA, WFNA or hydrogen peroxide.

2. General description of ionic liquids (ILs)

ILs are synthesized by reaction of a base with a strong acid. ILs are therefore salts and consist of negative and positive ions. It is generally accepted that the anion (negative ion) is more important in controlling the physical properties of the IL and that the nature of the cation (positive ion) affects the stability and reactivity of the IL. Therefore, it is possible to adjust physical properties by making changes to the structure of either the anion or the cation, or both, to suit requirements. Such strategies may also be of interest for designing energetic materials. Approximately 10^{18} different ionic liquids are possible (Trohalaki et al., (2005)). The number of ILs synthesized has expanded almost exponentially over the past two decades and it is certain that new classes will be developed in the forthcoming years, hence it is not practical to study experimentally the chemical activity of all of these innumerable ILs. Therefore, theoretical tools have been developed for some of the properties, and new tools need to be developed to predict remaining physicochemical properties of interest so as to allow for an efficient approach to screen and design ILs for the desired application. Applications of ILs are also numerous: electro-deposition of metals, fuel desulphurization, propellants, fuel cells, etc. However, to date only a handful of the proposed applications have

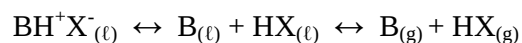
come to full fruition. By far the largest academic activity with ILs has been with their chemical synthesis. Data on some of the physiochemical properties of ILs can be found in our interim report # 1.

3. Chemical nature of vapor above ILs and above ILs-white fuming nitric acid (WFNA) mixtures

The chemical nature of the vapor above an ionic liquid is difficult to determine experimentally. It is, however, important to know how the vapor pressure forms over an ionic liquid surface. Four possibilities exist at equilibrium above the liquid phase; an ion-pair (including ion-pair clusters), separated ions, neutral pairs or separated neutrals. Experimental findings and theoretical calculations are reported in the literature on this issue. Ionic liquids can be divided into two classes: protic ionic liquids and aprotic ionic liquids.

3.1 Protic ionic liquids

According to Earle et al. (2006), an equilibrium exists between ionic and non-ionic species for protic ionic liquids:

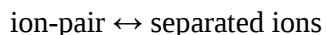


where (ℓ) represents the liquid phase and (g) represents the gas phase. Calculations made by Schmidt et al. (2005) on protic triazolium-based energetic ionic liquids show that the neutral pair is of lower energy than the ionic pair. However, separation of the molecules in the pair requires a significant amount of energy: about 50 kJ mol⁻¹. One of the conclusions of this paper is that the ionic pair once formed will transfer one proton to form a neutral pair. This

proton transfer is therefore fundamental for understanding the decomposition of protic triazolium-based species. However, Baranyai et al. (2004) do not observe the formation of species normally associated with the proton transfer process. Zorn et al. (2006) deduced from their calculations on protic tetrazolium-based ionic liquids that when a cation is paired with an oxygen rich anion, an isolated gas phase ion-pair was not generally found to be stable. In fact, a proton transfers without barrier from the cation to the anion to form a neutral pair. This result is consistent with the experimental findings of Leal et al. (2007), who report that the gas phase above a protic ionic liquid is composed of separated neutral molecules.

3.2 Aprotic ionic liquids

Calculations made by Emel'yanenko et al. (2007) on the gas phase equilibrium:



for 1-butyl-3-methylimidazolium dicyanamide indicate that the dissociation of the ion-pair is marginal. Experimental and theoretical works reported by Strasser et al. (2007) suggest that the vapor pressure of an aprotic ionic liquid (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) is composed of isolated ion pairs. The presence of clusters of ion pairs also seems to be negligible. This conclusion is supported by another experimental work performed by Leal et al. (2007), who find that the gas phase is composed of isolated ion pairs and that no experimental evidence supports the formation of ion clusters. Armstrong et al. (2007) performed the analysis of the vapor pressure of 1-ethyl-3-methylimidazolium ethylsulfate by mass spectrometry (MS). They deduced from their MS experiments that the vapor of these ionic liquids consists of ion pairs, although they do not observe directly these ion pairs because the ionized ion pairs (formed in the ionization chamber of the mass spectrometer by electron bombardment) are thought to be unstable and, therefore, undergo

fragmentation. One other finding of Armstrong et al. (2007) is that clusters of ion pairs do not seem to form in the gas phase.

3.3 Chemical nature of gases above ILs-WFNA liquid mixtures

One can expect to observe in the gas phase, nitric acid (with small amounts of NO_2) and other neutral molecules (neutral pairs or separated neutrals) according to subsections 3.1 and 3.2. Actually, Chambreau and Vaghjiani et al. (2008) showed that ILs and WFNA react exothermically in the liquid phase to form products in the liquid phase that then elute into the gas phase. This is further discussed in section 5.

4. Thermochemistry of imidazoles, triazoles and tetrazoles

Imidazole, triazole, and tetrazole compounds and their derivatives are interesting molecules because of their potential applications as explosives or propellants. As shown in section 3, these compounds are potentially interesting in the field of ionic liquids (ILs) because imidazolium, triazolium, and tetrazolium cations are frequently encountered in ILs. In fact, even for the simplest of these compounds, there is a general lack of good thermodynamics data sets that include the standard enthalpy of formation at 298.15 K, heat capacity (at constant pressure, C_p° or at constant volume, C_v°) for a wide range of temperatures, and the standard absolute entropy, S° . Such data is needed to carry out accurate kinetics modeling studies.

4.1 Estimation of thermodynamic data

Ab-initio methods have been shown to be reliable tools for estimating the thermochemistry of many compounds. Three methods of estimating the gas phase standard enthalpy of formation at 298.15 K have been proposed by the author of this report using quantum chemistry tools. Two of these methods can be applied to imidazole, triazole and tetrazole compounds. One of these methods is devoted to general organic compounds and the other to energetic materials with nitro and nitrate groups. The gas phase standard enthalpy of formation of molecule j at 298.15 K can be determined from the following equation:

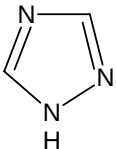
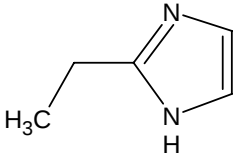
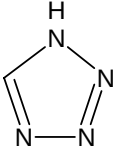
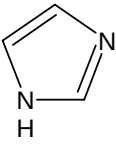
$$\Delta_f H^0_{298.15\text{ K (g)}} = 627.51 \times \left(E_j + ZPE_j + \text{thermal corrections} + \sum_i \alpha_i c_i^* \right)$$

where α_i is the number of atoms i in molecule j and c_i^* the atomic correction for atom i . E_j and ZPE_j denote, respectively, the absolute electronic energy and zero-point energy, calculated using either Gaussian 98W or GAUSSIAN 03 suite of programs. The units are Hartree molecule⁻¹ for E_j , ZPE_j and thermal corrections, and Hartree atom⁻¹ for c_i^* , whereas $\Delta_f H^0_{298.15\text{ K (g)}}$ is in kcal mol⁻¹. Three atomic corrections (C, H and N) are considered here for the method established for organic compounds and five atomic corrections (C, H, N, C_d, N_d) are considered for the method established for energetic compounds with one more atomic correction for hypervalent nitrogen (noted N_{hyp}) as encountered in nitroimidazoles, nitrotriazoles and nitrotetrazoles. C_p^0 , C_v^0 , and S^0 are calculated using statistical thermodynamic equations once the vibration frequencies and inertia moments have been estimated using the Gaussian software packages.

4.2 Results

Table 1 compares the experimental data and the calculated data with both methods, and Table 2 reports calculated gas phase standard enthalpy of formation at 298.15 K with both methods for compounds for which no experimental data is available.

Table 1. Comparison between experimental gas phase standard enthalpy of formation at 298.15 K, and calculated gas phase standard enthalpy of formation at 298.15 K for imidazoles, triazoles and tetrazoles.

Compound CAS Registry Number	Experimental $\Delta_f H^0_{298.15\text{ K (g)}}$ (kcal mol ⁻¹)	Calculated $\Delta_f H^0_{298.15\text{ K (g)}}$ with the method for organic compounds (kcal mol ⁻¹)	Calculated $\Delta_f H^0_{298.15\text{ K (g)}}$ with the method for energetic compounds (kcal mol ⁻¹)
1H-1,2,4-triazole 288-88-0 	46.1±0.2 45.05	40.7	43.4
2-ethyl-1H-imidazole 1072-62-4 	16.3±0.31	13.5	15.6
1H-tetrazole 288-94-8 	76.6±0.7	71.7	74.0
1H-imidazole 288-32-4 	33.29±0.45 30.6±1.8	29.1	32.3

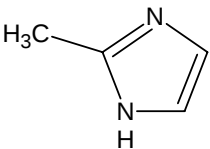
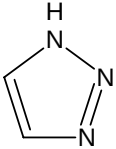
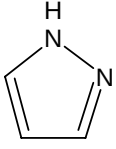
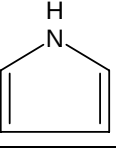
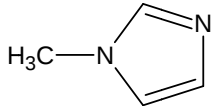
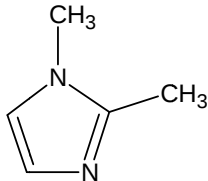
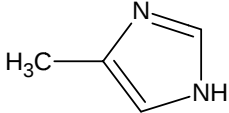
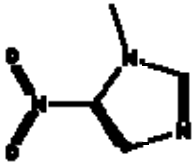
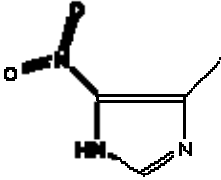
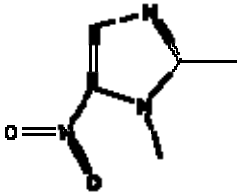
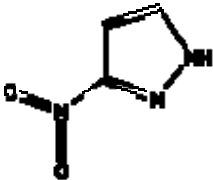
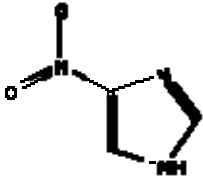
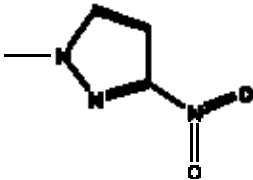
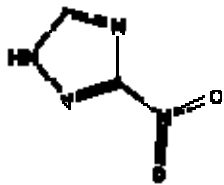
2-methyl-1H-imidazole 693-98-1 	21.5±0.26	18.5	21.1
1H-1,2,3-triazole 288-36-8 	59	57	59.7
1H-pyrazole 288-13-1 	42.9 43.3	39.2	42.4
Pyrrole 109-97-7 	25.9±0.1 34.23	26.4	30.0

Table 1 shows unambiguously that the method established for energetic compounds performs better than the method established for general organic compounds. This conclusion is interesting because this method has been established for nitro and nitrate compounds and therefore it can be expected to provide reasonably accurate results for nitroimidazoles, nitrotriazoles and nitrotetrazoles reported in Table 2. Calculations are computationally expensive and all of the results are not available at this time for most of the compounds reported in Table 2. Because of the importance of these compounds in the field of energetic materials, a complete data set of these results will be published in a journal article at a later date.

Table 2. Calculated gas phase standard enthalpy of formation at 298.15 K for imidazole, triazole and tetrazole compounds for which experimental data are not available.

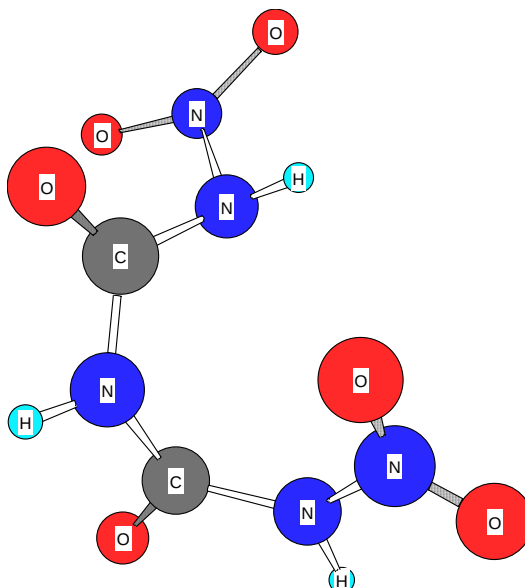
Compound CAS Registry Number	Experimental $\Delta_f H^0_{298.15\text{ K (g)}}$ (kcal mol ⁻¹)	Calculated $\Delta_f H^0_{298.15\text{ K (g)}}$ with the method for organic compounds (kcal mol ⁻¹)	Calculated $\Delta_f H^0_{298.15\text{ K (g)}}$ with the method for energetic compounds (kcal mol ⁻¹)
1-methyl-1H-imidazole 616-47-7 	-	26.2	28.9
1,2-dimethyl-1H-imidazole 1739-84-0 	-	16.3	18.4
4-methylimidazole 822-36-6 	-	19.6	22.2
1-Methyl-5-nitroimidazole 3034-42-2 	-		
4-methyl-5-nitroimidazole 14003-66-8 	-		

1,2-Dimethyl-5-nitroimidazole 551-92-8 	-		
3(5)-nitropyrazole 26621-44-3 	-		
4-nitro-1H-imidazole 3034-38-6 	-		
1-Methyl-5-nitropyrazole 54210-33-2 	-		
1-methyl-3-nitropyrazole 54210-32-1 	-		

3-nitro-1H-1,2,4-triazole 24807-55-4 	-		
1,5-diamino-1,2,3,4-tetrazole	-	90.6	99.8
4-amino-1,2,4-triazole	-	73.7	79.8

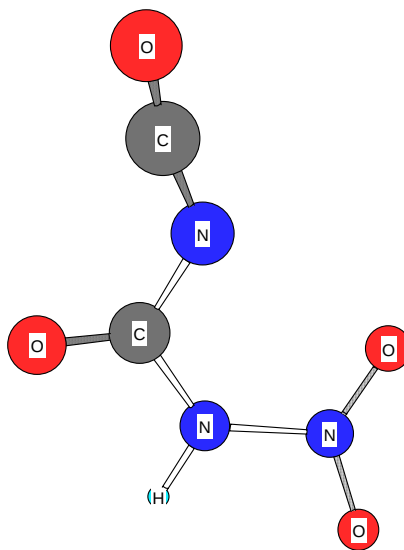
5. Thermochemistry of compounds formed during ILs-WFNA reaction

Chambreau and Vaghjani et al. (2008) recently presented experimental results on a class of ILs which exhibit hypergolicity at room temperature with WFNA. They presented mechanistic information on reactions in the liquid phase to explain the formation of species observed by Fourier transform infrared (FTIR) spectroscopy in the gas phase above the reacting ILs and WFNA mixtures. For 1-butyl-3-methyl imidazolium dicyanamide reacting with WFNA they observed in the gas phase; HNO_3 , CO_2 , N_2O and HNCO . Also present was water and NO_2 (WFNA contains some amount of NO_2). HNCO , N_2O and CO_2 were presumed to form from dinitrobiuret, $\text{NO}_2\text{NHCONHCONHNO}_2$ (abbreviated DNB),



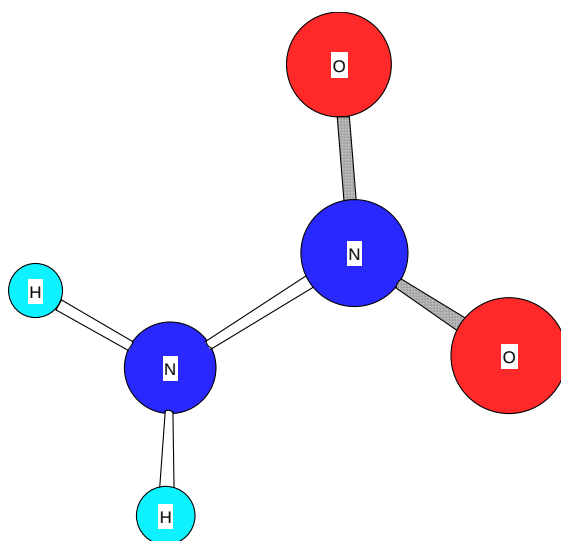
Sketch 1: molecular structure of DNB

which decomposes thermally to give $\text{NO}_2\text{NHCONCO}$ (or intermediate # 1, see below),



Sketch 2: molecular structure of intermediate #1

and NH_2NO_2 (or intermediate # 2, see below).



Sketch 3: molecular structure of intermediate #2

These two intermediates in the liquid phase, respectively, give $\text{HNCO} + \text{N}_2\text{O} + \text{CO}_2$ and $\text{N}_2\text{O} + \text{H}_2\text{O}$. These compounds together with HNO_3 and NO_2 from the WFNA will lead to ignition or not depending on the temperature and the concentration of the species reached in the gas phase. Since DNB, intermediate #1 and intermediate #2 are nitro compounds, their thermochemistry can be calculated by using the theoretical method established for nitro and nitrate compounds. However, these three compounds are not observed in the gas phase. It is therefore probably more logical to tentatively explain ignition by considering only those species that are actually observed in the gas phase namely; HNCO , N_2O , NO_2 , HNO_3 , H_2O and CO_2 .

5.1 Gas phase thermochemistry of DNB and of the intermediates

The gas phase thermochemistry of DNB can be calculated by using the method established for nitro compounds. The validation of this method was presented by Osmont et al. (2007). This procedure gives a value of $-47.9 \text{ kcal mol}^{-1}$ for the gas phase standard enthalpy of formation at

298.15K. Vibration frequencies and inertia moments have been computed to allow for the calculation of C_p° and S° over a wide temperature range. For intermediate # 2, or nitramide, the experimental data available are somewhat confusing. Burcat and Ruscic (2009) in the latest version of their thermodynamic database report two quite different values for the gas phase standard enthalpy of formation at 298.15 K: $-6.2 \pm 2.4 \text{ kcal mol}^{-1}$ and $-0.7 \text{ kcal mol}^{-1}$. Our method applied to NH_2NO_2 leads to a value of $+1.4 \pm 3.0 \text{ kcal mol}^{-1}$, which is more consistent with their latter number. Vibration frequencies and inertia moments have been computed to allow for the calculation of C_p° and S° over a wide temperature range. For intermediate # 1, a value of $-44.5 \text{ kcal mol}^{-1}$ is derived by using the same method as that for DNB and nitramide. As with the other compounds, vibration frequencies and inertia moments have been computed for intermediate # 1 to allow for the calculation of C_p° and S° over a wide temperature range.

5.2 Thermochemistry of HNCO, HNO₃, NO₂, N₂O, H₂O, and CO₂

Species present as reactants in the gas phase above reacting liquids are HNCO (isocyanic acid), nitric acid (HNO₃ or HONO₂), NO₂, N₂O, H₂O and CO₂. The thermochemistry of these small species are generally known and are reported in the CHEMKIN format by Burcat and Ruscic (2009) in their latest version of their thermodynamics database and are also reported below in the CHEMKIN format.

```
HNCO Isocyanic Acia 5/05H  1.N  1.C  1.0  1.G   200.000  6000.000  B  43.02478  1
  5.30045051E+00  4.02250821E-03-1.40962280E-06  2.23855342E-10-1.32499966E-14    2
-1.61995274E+04-3.11770684E+00  2.24009031E+00  1.45600497E-02-1.54352330E-05    3
  8.55535028E-09-1.79631611E-12-1.54589951E+04  1.21663775E+01-1.42642740E+04    4

HN03                T 8/03H  1.N  1.0  3.   0.G   200.000  6000.000  B  63.01288  1
```

8.03098942E+00	4.46958589E-03	-1.72459491E-06	2.91556153E-10	-1.80102702E-14	2
-1.93138183E+04	-1.62616537E+01	1.69329154E+00	1.90167702E-02	-8.25176697E-06	3
-6.06113827E-09	4.65236978E-12	-1.74198909E+04	1.71839838E+01	-1.61524852E+04	4
N02	L 7/88N	10	2	0	OG 200.000 6000.000 A 46.00554 1
0.48847540E+01	0.21723955E-02	-0.82806909E-06	0.15747510E-09	-0.10510895E-13	2
0.23164982E+04	-0.11741695E+00	0.39440312E+01	-0.15854290E-02	0.16657812E-04	3
-0.20475426E-07	0.78350564E-11	0.28966180E+04	0.63119919E+01	0.41124701E+04	4
N20	L 7/88N	20	1	0	OG 200.000 6000.000 A 44.01288 1
0.48230729E+01	0.26270251E-02	-0.95850872E-06	0.16000712E-09	-0.97752302E-14	2
0.80734047E+04	-0.22017208E+01	0.22571502E+01	0.11304728E-01	-0.13671319E-04	3
0.96819803E-08	-0.29307182E-11	0.87417746E+04	0.10757992E+02	0.98141682E+04	4
H2O	L 5/89H	20	1	0	OG 200.000 6000.000 A 18.01528 1
0.26770389E+01	0.29731816E-02	-0.77376889E-06	0.94433514E-10	-0.42689991E-14	2
-0.29885894E+05	0.68825500E+01	0.41986352E+01	-0.20364017E-02	0.65203416E-05	3
-0.54879269E-08	0.17719680E-11	-0.30293726E+05	-0.84900901E+00	-0.29084817E+05	4
CO2	L 7/88C	10	2	0	OG 200.000 6000.000 A 44.00980 1
0.46365111E+01	0.27414569E-02	-0.99589759E-06	0.16038666E-09	-0.91619857E-14	2
-0.49024904E+05	-0.19348955E+01	0.23568130E+01	0.89841299E-02	-0.71220632E-05	3
0.24573008E-08	-0.14288548E-12	-0.48371971E+05	0.99009035E+01	-0.47328105E+05	4

6. Calculations at thermodynamic equilibrium

For non-hypergolic systems, i.e. systems for which an external ignition device is required, chemical equilibrium calculations are often used to estimate flammability limits. From these equilibrium calculations, adiabatic flame temperatures are considered as a criterion to estimate lower and upper flammability limits, at a given total pressure. It has been shown that the

adiabatic flame temperature at the lower and upper flammability limits at a given pressure remains approximately constant in hydrocarbon/air mixtures and the reported experimental limits at atmospheric pressure correspond generally to adiabatic flame temperatures in the 1000-1500 K range. A criterion of 1200 K is often found convenient. It is therefore tenable that the flammability diagrams of hypergolic mixtures can be rationalized with such a thermochemical criterion. All these points were discussed in interim report # 2. A criterion of about 2000 K and above seems to be appropriate to discuss the occurrence of hypergolic ignition in a system. This simple thermochemical criterion is actually not sufficient and needs to be complemented by a detailed chemical kinetics model to prove that a system can be hypergolic under specified conditions. Concerning ionic liquids and WFNA, ignition has been observed in a gas phase mixture of HNCO, N₂O, NO₂, HNO₃, H₂O and CO₂ at unspecified conditions of temperature and pressure. The first task is to ascertain whether a mixture containing these species has the ability to sustain a flame. In the framework of interim report # 2, this task was developed in general terms and then specifically applied to the MMH/NTO hypergolic system. Such an analysis can also be performed here, but as in the case of MMH/NTO, the exact composition of the mixture in which ignition occurs is more than often not well characterized. Future studies at AFRL, Edwards AFB to determine the composition of such mixtures would be very valuable in the validation procedures discussed below.

Since the quantitative composition of the gas phase above the liquid is not known, and even if it can be considered qualitatively as known, the best approach to use here is to examine many mixtures at different initial conditions of pressure and temperature to determine if such mixtures are able to sustain a flame. The answer is necessarily yes, because ignition is experimentally observed (Chambreau and Vaghjiani et al. (2008)). It remains possible,

however, that an important species needed to quantitatively explain the observed ignition delay is presently unidentified and its nature must be identified to amend the initial detailed chemical kinetics model. For instance, species such as O_2 cannot be observed by using the FTIR technique.

6.1 Pure HNCO

A determination of whether pure HNCO is able to sustain a flame is an important exercise. The gas phase standard enthalpy of formation at 298.15 K of HNCO is about $-28 \text{ kcal mol}^{-1}$. This would generally indicate that the decomposition of such a molecule would be endothermic. This is, however, not true for some compounds, as is the case with certain organic peroxides and perchloric acid ($HClO_4$). Equilibrium calculations can shed some light in this area. For pure HNCO, adiabatic equilibrium calculations at constant pressure indicate that its thermal decomposition is exothermic as shown below:

	INITIAL STATE:	EQUILIBRIUM STATE:
P (atm)	1.0000E+00	1.0000E+00
T (K)	3.8000E+02	8.8078E+02
Mole Fractions		
HNCO	1.0000E+00	8.1567E-08
CO	0.0000E+00	4.1768E-01
CO2	0.0000E+00	8.2333E-02
H2O	0.0000E+00	8.2704E-03
CH4	0.0000E+00	9.0590E-02
H2	0.0000E+00	1.0580E-01
N2	0.0000E+00	2.9529E-01

At equilibrium, a temperature of about 880 K is predicted. Since this is lower than the 2000 K adiabatic flame temperature criterion, this probably means that pure HNCO is not able to sustain a decomposition flame. However, even if the initial chosen state is arbitrary, this calculation shows that the thermal decomposition of HNCO must be considered in the detailed chemical kinetics model. The associated exothermicity can possibly be the cause of ignition or, at least, an important parameter to consider. This can only be examined once a detailed chemical kinetics model is built.

6.2 Mixtures of HNCO and HNO₃

Here we examine the possibility that ignition is specifically due to HNCO-HNO₃ mixtures. A 50/50 mixture is chosen as a starting example.

	INITIAL STATE:	EQUILIBRIUM STATE:
P (atm)	1.0000E+00	1.0000E+00
T (K)	3.8000E+02	2.5090E+03
Mole Fractions		
HNCO	5.0000E-01	4.9302E-10
CO	0.0000E+00	2.5932E-02
O	0.0000E+00	5.6990E-03
H	0.0000E+00	1.7171E-03
CO ₂	0.0000E+00	2.5258E-01
NO	0.0000E+00	1.1339E-02
H ₂ O	0.0000E+00	2.6137E-01
HNO ₃	5.0000E-01	2.9272E-11
OH	0.0000E+00	2.4029E-02
H ₂	0.0000E+00	4.2509E-03

N2	0.0000E+00	2.7283E-01
O2	0.0000E+00	1.4022E-01
H2O	0.0000E+00	1.9371E-05

The adiabatic flame temperature at constant pressure is about 2500 K. This indicates that such a system is able to sustain a flame.

6.3 Mixtures of HNCO, CO₂, H₂O, and N₂O

By considering the equations given by Chambreau and Vaghjiani et al. (2008) for one mole of DNB decomposed in the liquid phase, there will be an equal amount of HNCO, CO₂, H₂O and twice this amount of N₂O in the gas phase. Such a mixture can probably lead to hypergolic ignition as shown below because an adiabatic temperature of about 2300 K is computed in which CO₂, H₂O, N₂ and O₂ represent about 97 mol% of the gases at thermodynamic equilibrium.

	INITIAL STATE:	EQUILIBRIUM STATE:
P (atm)	1.0000E+00	1.0000E+00
T (K)	3.8000E+02	2.2833E+03
Mole Fractions		
HNCO	2.0000E-01	2.4181E-10
N2O	4.0000E-01	1.9379E-07
CO	0.0000E+00	1.5069E-02
O	0.0000E+00	9.4194E-04
H	0.0000E+00	4.0470E-04
CO2	2.0000E-01	3.0131E-01
NO	0.0000E+00	4.9068E-03

H2O	2.0000E-01	2.3109E-01
OH	0.0000E+00	7.8783E-03
H2	0.0000E+00	2.0522E-03
N2	0.0000E+00	3.9302E-01
O2	0.0000E+00	4.3310E-02

N₂O is known to be an oxidant as well as a monergol, i.e. its decomposition is sufficiently exothermic that it is able to sustain a decomposition flame. Therefore, the thermal decomposition of N₂O must be included in the detailed chemical kinetics model. It can be supposed that for the present case, thermal decomposition of N₂O leads to the production of O atoms, through the spin-forbidden process, $\text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}$, and that ground-state O atoms then further react with HNCO. The former process is known to be the initiation step during thermal decomposition of pure N₂O.

6.4 Mixtures of HNCO, CO₂, H₂O, N₂O, HNO₃, and NO₂

The amount of HNO₃ in the gas phase will be related to the concentration of HNO₃ in the liquid solution of IL + WFNA at a given temperature. Raoult's law can be used for ideal solutions or activity coefficients can be used for non-ideal solutions to predict the composition. It should be noted that a mixture of WFNA and water was also used in some of the experiments performed by Chambreau and Vaghjiani et al. (2008). Moreover, small amounts of NO₂ are also present in WFNA. Presence of HNO₃ and NO₂ in the mixture allows for two oxidants to be considered.

	INITIAL STATE:	EQUILIBRIUM STATE:
P (atm)	1.0000E+00	1.0000E+00
T (K)	3.8000E+02	1.9195E+03

Mole Fractions

HNCO	1.6393E-01	1.1061E-12
CO	0.0000E+00	3.5231E-04
NO2	1.6393E-02	7.1443E-06
N2O	3.2787E-01	1.4522E-07
O	0.0000E+00	1.5090E-04
CO2	1.6393E-01	2.3066E-01
NO	0.0000E+00	3.8174E-03
H2O	1.6393E-01	2.2980E-01
HNO3	1.6393E-01	4.2070E-11
OH	0.0000E+00	2.2640E-03
N2	0.0000E+00	3.5039E-01
O2	0.0000E+00	1.8247E-01

In this case, the adiabatic flame temperature at constant pressure is about 2000 K and CO₂, H₂O, N₂ and O₂ constitute about 99.3 mol% of the gases at thermodynamic equilibrium. A mixture with this composition is probably able to sustain a flame.

7. Detailed chemical kinetics model

7.1 Introduction

It seems clear, from the analyses presented in section 6, that the species identified in the gas phase namely; HNCO, HNO₃, N₂O, NO₂, CO₂, and H₂O are able to sustain a flame. However, thermodynamics calculations at equilibrium alone do not explain by which chemical pathway(s) ignition occurs. Elucidation of these pathways is relevant to the

development of a detailed chemical kinetics model, and such a model is needed to understand the chemical reactivity of a system when time is a parameter of the problem. Data of interest which can be estimated with a detailed chemical kinetics model are ignition times and species time profiles during the ignition delay. Species profiles may also be determined when there is no ignition in the system. In fact, depending on several other parameters such as composition, temperature, and pressure, there will be a finite time to reach equilibrium from a given initial state of the system under consideration.

7.2 Building of a detailed chemical kinetics model

It is beyond the scope of this work to present all of the features and considerations of the field of chemical kinetics. Some of the important facts are discussed below. A detailed chemical kinetics model is composed of many reactions depending on the number of reactants and the number of atoms in the molecules. The chemical nature of the atoms involved is also important. All these reactions are considered to be elementary. They can be unimolecular, bimolecular or termolecular. Unimolecular and termolecular reactions are pressure-dependent and there are several mathematical methods to treat them. A detailed chemical kinetics model will have initiation reactions, chain branching reactions, chain propagation reactions and chain termination reactions. From the results of the previous section, it can be concluded that the thermal decomposition of HNCO, HNO₃ and N₂O must be written in detail to account for the observed exothermicity, and also because of the subsequent production of additional reactive species in these processes. The atoms and radicals formed during the three corresponding initiation reactions will interact with the remaining HNCO, HNO₃, and N₂O, and also with the any other species present in the system such as H₂O, CO₂ and NO₂. The radical species, NO₂ will also be available for reactions in the system. Once all of the feasible reactions are

written, at least as best as possible, a rate constant, k , needs to be specified for each of the reaction steps. Depending on the availability of thermodynamics/kinetics databases a value of k may be uniquely assignable. k is generally considered to follow the Arrhenius equation:

$$k = A e^{\frac{-E}{RT}}$$

where A represents the frequency (or pre-exponential) factor, E the activation energy, R the perfect gas constant and T the temperature. However, the A factor also has a temperature dependence, which generally cannot be neglected for accurate combustion predictions and therefore, a modified-Arrhenius equation is often needed:

$$k = A T^n e^{\frac{-E}{RT}}$$

The following pages report our initial detailed chemical kinetics model relevant to the present system. The model consists of 61 species and 377 reactions. Rate constants are from available compilations and in some cases have been estimated by analogy with similar reactions. Units used are; $E(\text{cal mol}^{-1})$, $T(\text{K})$, $R(\text{cal mol}^{-1} \text{K}^{-1})$, and $A(\text{cm}^3 \text{mol}^{-1} \text{s}^{-1})$.

		C							
		P H							
		H A							
		A R							
SPECIES		S G	MOLECULAR	TEMPERATURE		ELEMENT			COUNT
CONSIDERED		E E	WEIGHT	LOW	HIGH	C	H	N	O

1.	HNCO	G 0	43.02522	200.0	6000.0	1	1	1	1
2.	NCO	G 0	42.01725	300.0	4000.0	1	0	1	1
3.	N	G 0	14.00670	200.0	6000.0	0	0	1	0
4.	CO	G 0	28.01055	200.0	6000.0	1	0	0	1
5.	NO2	G 0	46.00550	200.0	6000.0	0	0	1	2
6.	N2O	G 0	44.01280	200.0	6000.0	0	0	2	1
7.	O	G 0	15.99940	200.0	6000.0	0	0	0	1
8.	C	G 0	12.01115	200.0	6000.0	1	0	0	0
9.	H	G 0	1.00797	200.0	6000.0	0	1	0	0
10.	CO2	G 0	44.00995	200.0	6000.0	1	0	0	2
11.	NO	G 0	30.00610	200.0	6000.0	0	0	1	1
12.	H2O	G 0	18.01534	200.0	6000.0	0	2	0	1
13.	NH2NO2	G 0	62.02814	200.0	6000.0	0	2	2	2
14.	HN03	G 0	63.01287	200.0	6000.0	0	1	1	3
15.	HONO	G 0	47.01347	200.0	6000.0	0	1	1	2
16.	NH	G 0	15.01467	200.0	6000.0	0	1	1	0
17.	HNO	G 0	31.01407	200.0	6000.0	0	1	1	1
18.	NH2	G 0	16.02264	200.0	3000.0	0	2	1	0
19.	OH	G 0	17.00737	200.0	6000.0	0	1	0	1

20.	CH3	G 0	15.03506	300.0	5000.0	1	3	0	0
21.	CH4	G 0	16.04303	200.0	6000.0	1	4	0	0
22.	H2	G 0	2.01594	300.0	5000.0	0	2	0	0
23.	NH3	G 0	17.03061	300.0	5000.0	0	3	1	0
24.	N2	G 0	28.01340	300.0	5000.0	0	0	2	0
25.	CN	G 0	26.01785	300.0	5000.0	1	0	1	0
26.	O2	G 0	31.99880	300.0	5000.0	0	0	0	2
27.	NO3	G 0	62.00490	300.0	5000.0	0	0	1	3
28.	H02	G 0	33.00677	300.0	5000.0	0	1	0	2
29.	H2O2	G 0	34.01474	300.0	5000.0	0	2	0	2
30.	N2O4	G 0	92.01100	300.0	5000.0	0	0	2	4
31.	CH3O	G 0	31.03446	300.0	3000.0	1	3	0	1
32.	CH	G 0	13.01912	300.0	5000.0	1	1	0	0
33.	HCO	G 0	29.01852	300.0	5000.0	1	1	0	1
34.	HOCO	G 0	45.01792	300.0	4000.0	1	1	0	2
35.	CHCO	G 0	41.02967	300.0	4000.0	2	1	0	1
36.	CH2S	G 0	14.02709	300.0	4000.0	1	2	0	0
37.	CH2T	G 0	14.02709	200.0	6000.0	1	2	0	0
38.	CH2O	G 0	30.02649	300.0	5000.0	1	2	0	1
39.	CH3OH	G 0	32.04243	300.0	5000.0	1	4	0	1
40.	CH3O2	G 0	47.03386	300.0	5000.0	1	3	0	2
41.	CH2OH	G 0	31.03446	250.0	4000.0	1	3	0	1
42.	CH3CHO	G 0	44.05358	300.0	5000.0	2	4	0	1
43.	C2H	G 0	25.03027	300.0	4000.0	2	1	0	0
44.	C2H2	G 0	26.03824	300.0	5000.0	2	2	0	0
45.	N2H2	G 0	30.02934	300.0	5000.0	0	2	2	0
46.	HCN	G 0	27.02582	300.0	4000.0	1	1	1	0
47.	NNH	G 0	29.02137	250.0	4000.0	0	1	2	0
48.	C2H4	G 0	28.05418	300.0	5000.0	2	4	0	0
49.	C2H5	G 0	29.06215	300.0	5000.0	2	5	0	0
50.	CH2CO	G 0	42.03764	300.0	5000.0	2	2	0	1
51.	CH3O2H	G 0	48.04183	200.0	6000.0	1	4	0	2
52.	C2H3	G 0	27.04621	300.0	5000.0	2	3	0	0
53.	CH3CO	G 0	43.04561	300.0	5000.0	2	3	0	1
54.	HCCOH	G 0	42.03764	300.0	4000.0	2	2	0	1
55.	CH3NH	G 0	30.04973	300.0	5000.0	1	4	1	0
56.	CH2NH	G 0	29.04176	200.0	6000.0	1	3	1	0
57.	C2H6	G 0	30.07012	300.0	4000.0	2	6	0	0
58.	H2CN	G 0	28.03379	300.0	4000.0	1	2	1	0
59.	HOCN	G 0	43.02522	300.0	4000.0	1	1	1	1
60.	C2N2	G 0	52.03570	300.0	5000.0	2	0	2	0
61.	HNNO	G 0	45.02077	300.0	4000.0	0	1	2	1

REACTIONS CONSIDERED	(k = A T**b exp(-E/RT))		
	A	b	E
1. HNC0+M=NH+CO+M	1.30E+16	0.0	84368.0
2. HNC0+H=NH2+CO	3.60E+04	2.5	2344.0
3. HNC0+O=HN0+CO	1.70E+06	2.1	0.0
4. HNC0+O=NH+CO2	1.70E+06	2.1	0.0
5. HNC0+OH=NH2+CO2	6.30E+10	-0.1	11643.0
6. HNC0+OH=NC0+H2O	5.20E+10	0.0	17565.0
Declared duplicate reaction...			
7. HNC0+H=NC0+H2	1.80E+05	2.4	9915.0
8. HNC0+O=NC0+OH	3.10E+06	1.9	6457.0
9. HNC0+OH=NC0+H2O	3.60E+07	1.5	3596.0
Declared duplicate reaction...			
10. HNC0+CH3=NC0+CH4	1.00E+12	0.0	9935.0
11. HNC0+NH2=NC0+NH3	1.00E+12	0.0	8941.0
12. HNC0+NH=NC0+NH2	1.00E+12	0.0	8941.0
13. HNC0+NO2=NC0+HONO	1.00E+12	0.0	8941.0
14. NC0+NO2=CO+NO+NO	2.10E+11	0.0	-874.0
15. NC0+NO2=CO2+N2O	2.30E+12	0.0	-874.0
16. NC0+OH=H+CO+NO	8.30E+12	-0.1	18041.0
17. NC0+N=N2+CO	3.30E+13	0.0	0.0

18.	NC0+H=NH+CO		5.20E+13	0.0	0.0
19.	NC0+O=N+CO2		8.00E+12	0.0	2503.0
20.	NC0+O=NO+CO		4.20E+13	0.0	0.0
21.	NC0+M=N+CO+M		3.30E+14	0.0	54046.0
22.	NC0+NO=N2O+CO		6.20E+17	-1.7	765.0
23.	NC0+NO=CO2+N2		7.80E+17	-1.7	765.0
24.	HONO+M=OH+NO+M		2.00E+31	-4.6	51175.0
25.	HONO+H=H2+NO2		2.00E+08	1.6	6616.0
26.	HONO+H=H2O+NO		8.10E+06	1.9	3844.0
27.	HONO+H=OH+HNO		5.60E+10	0.9	4967.0
28.	HONO+O=OH+NO2		1.70E+08	1.5	3030.0
29.	HONO+OH=H2O+NO2		1.20E+06	2.0	-596.0
30.	HONO+CH3=NO2+CH4		8.10E+05	1.9	5504.0
31.	HONO+NH2=NO2+NH3		9.20E+05	1.9	1917.0
32.	HNO+M=H+NO+M		2.60E+16	0.0	48681.0
33.	HNO+OH=NO+H2O		1.30E+07	1.9	-953.0
34.	HNO+H=H2+NO		4.50E+11	0.7	655.0
35.	HNO+H=O+NH2		3.50E+15	-0.3	29268.0
36.	HNO+O=OH+NO		4.50E+11	0.7	655.0
37.	HNO+NH2=NH3+NO		9.20E+05	1.9	-1152.0
38.	HNO+NO2=HONO+NO		9.20E+05	1.9	-1152.0
39.	HNO+NO=N2O+OH		8.50E+12	0.0	29586.0
40.	HNO+CH3=NO+CH4		8.20E+05	1.9	953.0
41.	NO+C=CO+N		1.70E+13	0.0	0.0
42.	NO+C=CN+O		1.10E+13	0.0	0.0
43.	NO2+H=NO+OH		1.30E+14	0.0	357.0
44.	NO2+O=NO+O2		3.90E+12	0.0	-238.0
45.	NO2+M=NO+O+M		5.70E+15	0.0	59987.0
46.	NO2+NH2=N2O+H2O		1.50E+16	-1.4	268.0
47.	NO+M=N+O+M		1.40E+15	0.0	148428.0
48.	N2O+M=N2+O+M		5.70E+14	0.0	56093.0
49.	N2O+O=N2+O2		1.40E+12	0.0	10809.0
50.	N2O+O=NO+NO		2.90E+13	0.0	23148.0
51.	NH2+NO2=NH2NO2		5.60E+48	-11.3	11882.0
52.	HONO+HONO=H2O+NO+NO2		3.49E-01	3.6	12138.6
53.	CH3O+NO=CH2O+HNO		8.40E+12	0.0	2050.0
54.	CH3+HO2=CH3O+OH		2.28E+13	0.0	0.0
55.	NO2+NO2=NO+NO+O2		1.60E+12	0.0	26123.0
56.	NO2+NO2=NO3+NO		9.60E+09	0.7	20900.0
57.	OH+NO2(+M)=HNO3(+M)		1.37E+15	-0.6	0.0
	Low pressure limit:	0.14200E+26 -0.29000E+01	0.00000E+00		
58.	HNO+HNO=N2O+H2O		4.00E+12	0.0	5000.0
59.	CH3+NO2=CH3O+NO		1.30E+13	0.0	0.0
60.	N2O4(+M)=NO2+NO2(+M)		4.05E+18	-1.1	12840.0
	Low pressure limit:	0.19600E+29 -0.38000E+01	0.12840E+05		
61.	NO2+HONO=NO+HNO3		6.03E+01	0.0	0.0
62.	N2O4+H2O=HONO+HNO3		2.52E+14	0.0	11586.0
63.	H+O+M=OH+M		6.20E+16	-0.6	0.0
64.	H+O2=OH+O		1.59E+17	-0.9	16873.8
65.	H2+O=OH+H		3.87E+04	2.7	6262.0
66.	H2+OH=H2O+H		2.16E+08	1.5	3441.7
67.	OH+OH=O+H2O		2.10E+08	1.4	-396.8
68.	O+O+M=O2+M		1.00E+17	-1.0	0.0
	H2	Enhanced by	2.900E+00		
	O2	Enhanced by	1.200E+00		
	N2	Enhanced by	1.200E+00		
	H2O	Enhanced by	1.850E+01		
	CO	Enhanced by	2.100E+00		
	CO2	Enhanced by	4.300E+00		
69.	H+OH+M=H2O+M		8.40E+21	-2.0	0.0
	H2	Enhanced by	1.900E+00		
	O2	Enhanced by	2.600E+00		
	N2	Enhanced by	2.600E+00		
	H2O	Enhanced by	9.500E+00		
	CO	Enhanced by	2.600E+00		
	CO2	Enhanced by	2.600E+00		
70.	H+O2+M=HO2+M		7.00E+17	-0.8	0.0
71.	HO2+H=OH+OH		1.50E+14	0.0	1003.8

72.	H02+H=H2+O2			2.50E+13	0.0	693.1
73.	H02+H=H2O+O			5.00E+12	0.0	1410.1
74.	H02+O=O2+OH			2.00E+13	0.0	0.0
75.	H02+OH=H2O+O2			6.02E+13	0.0	0.0
76.	H02+H02=H2O2+O2			4.20E+14	0.0	11981.6
77.	H2O2+M=OH+OH+M			1.00E+17	0.0	45411.1
	H2	Enhanced by	2.900E+00			
	O2	Enhanced by	1.200E+00			
	N2	Enhanced by	1.200E+00			
	H2O	Enhanced by	1.850E+01			
	CO	Enhanced by	2.100E+00			
	CO2	Enhanced by	4.300E+00			
78.	H2O2+H=H02+H2			1.70E+12	0.0	3752.4
79.	H2O2+H=H2O+OH			1.00E+13	0.0	3585.1
80.	H2O2+O=H02+OH			2.80E+13	0.0	6405.3
81.	H2O2+OH=H2O+H02			7.00E+12	0.0	1434.0
82.	CO+OH(+M)=CO2+H(+M)			2.45E-03	3.7	-1242.8
	Low pressure limit:	0.11700E+08	0.13500E+01	-0.71700E+03		
83.	CO+H02=CO2+OH			1.50E+14	0.0	23589.8
84.	CO+O+M=CO2+M			3.01E+14	0.0	3011.5
	O2	Enhanced by	1.200E+01			
	N2	Enhanced by	2.000E+00			
	CO	Enhanced by	3.000E+00			
	CO2	Enhanced by	7.000E+00			
85.	CO+O2=CO2+O			2.50E+12	0.0	47801.1
86.	HCO+M=CO+H+M			1.86E+17	-1.0	16993.3
	H2	Enhanced by	1.870E+00			
	N2	Enhanced by	9.900E-01			
	O2	Enhanced by	9.900E-01			
87.	HOCO(+M)=CO2+H(+M)			1.74E+12	0.3	32935.0
	Low pressure limit:	0.22900E+27	-0.30200E+01	0.35062E+05		
88.	HOCO(+M)=CO+OH(+M)			5.89E+12	0.5	33986.6
	Low pressure limit:	0.21900E+24	-0.18900E+01	0.35277E+05		
89.	CHCO+M=CO+CH+M			6.00E+15	0.0	58819.3
90.	CH+O=CO+H			1.00E+14	0.0	0.0
91.	CH+OH=HCO+H			3.00E+13	0.0	0.0
92.	CH+O2=CO+OH			2.00E+13	0.0	0.0
93.	CH2S+O=CO+H+H			1.50E+13	0.0	0.0
94.	CH2S+O=CO+H2			1.50E+13	0.0	0.0
95.	CH2S+OH=CH2O+H			3.00E+13	0.0	0.0
96.	CH2S+O2=CO+OH+H			3.10E+13	0.0	0.0
97.	CH2T+O=CO+H+H			5.00E+13	0.0	0.0
98.	CH2T+OH=CH+H2O			1.13E+07	2.0	3011.5
99.	CH2T+OH=CH2O+H			2.50E+13	0.0	0.0
100.	CH2T+O2=CO2+H+H			1.60E+12	0.0	1003.8
101.	CH2T+O2=CH2O+O			5.00E+13	0.0	9010.5
102.	CH2T+O2=CO2+H2			6.90E+11	0.0	501.9
103.	CH2T+O2=CO+OH+H			8.60E+10	0.0	-501.9
104.	CH2T+O2=HCO+OH			4.30E+10	0.0	-501.9
105.	CH3+O=CH2O+H			8.43E+13	0.0	0.0
106.	CH3+OH=CH2O+H2			8.00E+12	0.0	0.0
107.	CH3+OH=CH2T+H2O			1.13E+06	2.1	2437.8
108.	CH3+O2=CH2O+OH			5.20E+13	0.0	34894.8
109.	CH3+O2=CH3O2			1.70E+60	-15.1	18785.8
110.	CH3+HCO=CH4+CO			3.20E+11	0.5	0.0
111.	CH3OH=CH3+OH			2.80E+32	-5.0	97992.3
112.	CH4+H02=CH3+H2O2			4.48E+13	0.0	24641.5
113.	CH3+H02=CH4+O2			1.00E+12	0.0	0.0
114.	CH4+O=CH3+OH			1.90E+09	1.4	8675.9
115.	CH4+OH=CH3+H2O			1.50E+06	2.1	2437.8
116.	HCO+H=H2+CO			7.23E+13	0.0	0.0
117.	HCO+O=OH+CO			3.00E+13	0.0	0.0
118.	HCO+O=H+CO2			3.00E+13	0.0	0.0
119.	HCO+OH=H2O+CO			1.00E+14	0.0	0.0
120.	HCO+O2=H02+CO			4.20E+12	0.0	0.0
121.	HCO+HCO=CH2O+CO			2.00E+13	0.0	0.0
122.	CH2O+M=HCO+H+M			5.00E+16	0.0	76481.8
	H2	Enhanced by	2.900E+00			

	O2	Enhanced by	1.200E+00			
	N2	Enhanced by	1.200E+00			
	H2O	Enhanced by	1.850E+01			
	CO	Enhanced by	2.100E+00			
	CO2	Enhanced by	4.300E+00			
123.	CH2O+O2=HCO+H2O			1.00E+14	0.0	39914.0
124.	CH3CHO=HCO+CH3			2.00E+15	0.0	79110.9
125.	HCO+CH3OH=CH2O+CH2OH			9.60E+03	2.9	13097.5
126.	CH2O+H=HCO+H2			1.26E+08	1.6	2175.0
127.	CH2O+O=HCO+OH			3.50E+13	0.0	3513.4
128.	CH2O+OH=HCO+H2O			3.62E+05	2.5	-980.0
129.	CH2O+H2O2=HCO+H2O2			4.00E+11	0.0	8006.7
130.	CH2O+CH3=HCO+CH4			8.91E-13	7.4	-956.0
131.	CH2O+M=CO+H2+M			8.20E+15	0.0	69550.7
	H2	Enhanced by	2.900E+00			
	O2	Enhanced by	1.200E+00			
	N2	Enhanced by	1.200E+00			
	H2O	Enhanced by	1.850E+01			
	CO	Enhanced by	2.100E+00			
	CO2	Enhanced by	4.300E+00			
132.	CH3O+M=CH2O+H+M			1.96E+37	-6.7	33269.6
	H2	Enhanced by	2.900E+00			
	O2	Enhanced by	1.200E+00			
	N2	Enhanced by	1.200E+00			
	H2O	Enhanced by	1.850E+01			
	CO	Enhanced by	2.100E+00			
	CO2	Enhanced by	4.300E+00			
133.	CH2OH+M=CH2O+H+M			1.54E+13	0.0	33054.5
	H2	Enhanced by	2.900E+00			
	O2	Enhanced by	1.200E+00			
	N2	Enhanced by	1.200E+00			
	H2O	Enhanced by	1.850E+01			
	CO	Enhanced by	2.100E+00			
	CO2	Enhanced by	4.300E+00			
134.	CH2OH+H=CH3+OH			9.64E+13	0.0	0.0
135.	CH2OH+H=CH2O+H2			3.00E+13	0.0	0.0
136.	CH2OH+O=CH2O+OH			5.00E+12	0.0	0.0
137.	CH2OH+OH=CH2O+H2O			5.00E+12	0.0	0.0
138.	CH2OH+H2O2=CH2O+H2O2			1.20E+13	0.0	0.0
139.	CH2OH+CH3=CH2O+CH4			2.40E+12	0.0	0.0
140.	CH2OH+HCO=CH2O+CH2O			1.80E+14	0.0	0.0
141.	CH2OH+HCO=CH3OH+CO			1.20E+14	0.0	0.0
142.	CH2OH+O2=CH2O+H2O			1.80E+13	0.0	788.7
143.	CH2OH+H2O2=CH3OH+H2O			3.01E+09	0.0	2581.3
144.	CH3OH+O2=CH2OH+H2O			2.00E+13	0.0	44909.2
145.	CH3+OH=CH3O+H			5.74E+12	-0.2	13934.0
146.	CH3+O2=CH3O+O			4.30E+13	0.0	30807.8
147.	CH3O+H=CH2O+H2			2.00E+13	0.0	0.0
148.	CH3O+O=CH2O+OH			5.00E+12	0.0	0.0
149.	CH3O+OH=CH2O+H2O			5.00E+12	0.0	0.0
150.	CH3O+O2=CH2O+H2O			4.28E-13	7.6	-3537.3
151.	CH3O+H2O2=CH2O+H2O2			1.20E+13	0.0	0.0
152.	CH3O+CH3=CH4+CH2O			2.41E+13	0.0	0.0
153.	CH3O+CH2O=HCO+CH3OH			1.15E+11	0.0	1290.6
154.	CH3O2H=CH3O+OH			6.46E+14	0.0	42997.1
155.	CH3OH+OH=CH2OH+H2O			1.77E+04	2.6	-884.3
156.	CH3OH+OH=CH3O+H2O			1.77E+04	2.6	-884.3
157.	CH3OH+H=CH2OH+H2			3.20E+13	0.0	6094.6
158.	CH3OH+H=CH3O+H2			8.00E+12	0.0	6094.6
159.	CH3OH+H=CH3+H2O			5.25E+12	0.0	5329.8
160.	CH3OH+O=CH2OH+OH			3.88E+05	2.5	3083.2
161.	CH3OH+CH3O=CH2OH+CH3OH			1.51E+12	0.0	7002.9
162.	CH3OH+C2H3=CH2OH+C2H4			3.20E+01	3.2	7170.2
163.	CH3O2+H=CH3O+OH			9.60E+13	0.0	0.0
164.	CH3O2+O=CH3O+O2			3.60E+13	0.0	0.0
165.	CH3O2+OH=CH3OH+O2			6.00E+13	0.0	0.0
166.	CH3O2+H2O2=CH3O2H+O2			4.60E+10	0.0	-2581.3
167.	CH3O2+HCO=CH3O+H+CO2			3.00E+13	0.0	0.0

168.	CH302+CH3=CH30+CH30	2.00E+13	0.0	0.0
169.	CH302+H202=CH302H+H02	2.40E+12	0.0	9942.6
170.	CH302+CH20=CH302H+HCO	2.00E+12	0.0	11663.5
171.	CH302+CH302=CH30+CH30+02	7.80E+10	0.0	0.0
172.	CH302+CH302=CH30H+CH20+02	1.30E+11	0.0	0.0
173.	CH302+CH4=CH302H+CH3	1.80E+11	0.0	18475.1
174.	CH302+H2=CH302H+H	3.00E+13	0.0	26027.7
175.	CH302+CH30H=CH302H+CH20H	1.80E+11	0.0	13719.0
176.	CH302H+0H=CH302+H20	7.00E+12	0.0	1434.0
177.	CH302H+0=CH302+0H	2.80E+13	0.0	6405.3
178.	C2H+0=CO+CH	1.00E+13	0.0	0.0
179.	C2H+0H=CHCO+H	2.00E+13	0.0	0.0
180.	C2H+02=CHCO+0	6.02E+11	0.0	0.0
181.	C2H+02=CH+CO2	4.50E+15	0.0	25095.6
182.	C2H+02=HCO+CO	2.41E+12	0.0	0.0
183.	C2H2+0H=C2H+H20	2.71E+13	0.0	10492.3
184.	CHCO+H=CH2S+CO	1.50E+14	0.0	0.0
185.	CHCO+0=CO+CO+H	1.00E+14	0.0	0.0
186.	C2H2+0=CH2T+CO	7.81E+03	2.8	501.9
187.	C2H2+0=CHCO+H	1.39E+04	2.8	501.9
188.	C2H2+0H=HCCOH+H	5.06E+05	2.3	13503.8
189.	C2H2+0H=CH2CO+H	2.19E-04	4.5	-1003.8
190.	C2H2+0H=CH3+CO	4.85E-04	4.0	-2007.6
191.	HCCOH+H=CH2CO+H	1.00E+13	0.0	0.0
192.	CH2CO+H=CHCO+H2	3.00E+13	0.0	8604.2
193.	CH2CO+0=HCO+HCO	1.00E+13	0.0	5975.1
194.	CH2CO+0H=CHCO+H20	1.00E+13	0.0	2629.0
195.	CH2CO=CH2T+CO	3.00E+14	0.0	70984.7
196.	C2H3+0H=C2H2+H20	4.00E+12	0.0	0.0
197.	C2H3+0=CH2CO+H	3.00E+13	0.0	0.0
198.	C2H3+02=CH20+HCO	3.98E+12	0.0	-239.0
199.	CH3CO+H=CH2CO+H2	2.00E+13	0.0	0.0
200.	CH3CO+0=CH3+CO2	2.00E+13	0.0	0.0
201.	CH3CO+CH302=CH3+CO2+CH30	2.40E+13	0.0	0.0
202.	C2H4+H02=C2H3+H202	1.12E+13	0.0	30425.4
203.	C2H4+02=C2H3+H02	3.98E+13	0.0	61496.2
204.	C2H3+CH30H=C2H4+CH30	1.40E+01	3.1	6931.2
205.	C2H4+0=CH3+HCO	1.60E+08	1.4	525.8
206.	C2H4+0=CH3CO+H	1.60E+08	1.4	525.8
207.	C2H4+0=C2H3+0H	7.11E+08	1.6	7480.9
208.	C2H4+0H=C2H3+H20	9.70E+06	1.9	2361.4
209.	CH3CHO+H=CH3CO+H2	4.00E+13	0.0	4206.5
210.	CH3CHO+0=CH3CO+0H	5.00E+12	0.0	1792.5
211.	CH3CHO+0H=CH3CO+H20	1.00E+13	0.0	0.0
212.	CH3CHO+CH3=CH3CO+CH4	8.50E+10	0.0	6000.0
213.	CH3+CH20H=C2H5+0H	1.37E+14	-0.4	6596.6
214.	C2H5+0=CH20+CH3	4.24E+13	0.0	0.0
215.	C2H5+0=CH3CHO+H	5.32E+13	0.0	0.0
216.	C2H5+0=C2H4+0H	3.06E+13	0.0	0.0
217.	C2H5+02=C2H4+H02	2.00E+12	0.0	4995.2
218.	C2H5+CH30H=C2H6+CH20H	3.20E+01	3.2	9153.9
219.	C2H6+CH302=C2H5+CH302H	3.00E+11	0.0	14937.9
220.	C2H6+H02=C2H5+H202	1.70E+13	0.0	20458.9
221.	C2H6+02=C2H5+H02	3.98E+13	0.0	50908.2
222.	C2H6+0=C2H5+0H	1.40E+00	4.3	2772.5
223.	C2H6+0H=C2H5+H20	2.20E+07	1.9	1123.3
224.	C2H5+CH30H=C2H6+CH30	1.40E+01	3.1	8938.8
225.	NH3+M=NH2+H+M	1.40E+16	0.1	90600.0
	H20			
	N2	Enhanced by	6.500E+00	
		Enhanced by	4.000E-01	
226.	NH3+0H=NH2+H20	2.04E+06	2.0	566.0
227.	NH3+0=NH2+0H	2.10E+13	0.0	9000.0
228.	NH2+0H=NH+H20	9.00E+07	1.5	-457.0
229.	NH2+0=NH+0H	7.00E+12	0.0	0.0
230.	NH2+N0=N2+H20	3.00E+20	-2.6	924.0
231.	NH+0=N0+H	7.00E+13	0.0	0.0
232.	NH+0H=N+H20	2.00E+09	1.2	6.0
233.	NH+0H=HNO+H	4.00E+13	0.0	0.0

234.	NH+O2=N0+OH	1.00E+13	-0.2	4800.0
235.	NH+N0=N20+H	2.40E+15	-0.8	0.0
236.	N+O2=N0+O	6.40E+09	1.0	6279.9
237.	N+OH=N0+H	3.80E+13	0.0	0.0
238.	N+N0=N2+O	3.30E+12	0.3	0.0
239.	N0+H02=N02+OH	2.11E+12	0.0	-479.0
240.	N02=N0+O	7.60E+18	-1.3	73290.0
241.	N2H2+O=NH2+N0	1.00E+13	0.0	0.0
242.	N2H2+O=NNH+OH	2.00E+13	0.0	1000.0
243.	N2H2+OH=NNH+H2O	1.00E+13	0.0	1000.0
244.	N2H2+N0=NH2+N2O	3.00E+12	0.0	0.0
245.	NNH+OH=N2+H2O	5.00E+13	0.0	0.0
246.	N0+NNH=N2+HNO	2.00E+12	0.0	0.0
247.	NH2+N0=NNH+OH	1.39E+12	0.0	0.0
248.	N2O+H=N2+OH	9.60E+13	0.0	15100.0
249.	N2O+OH=N2+H02	2.00E+12	0.0	10000.0
250.	NH2+O2=HNO+OH	1.51E+12	-3.9	36100.0
251.	NH+O2=HNO+O	4.61E+05	2.0	6500.0
252.	N02+O=N03	1.32E+13	0.0	0.0
253.	N03+O=N02+O2	6.03E+12	0.0	0.0
254.	N03+OH=N02+H02	1.39E+13	0.0	0.0
255.	N03+H=N02+OH	6.62E+13	0.0	0.0
256.	HNO+O2=N0+H02	3.16E+12	0.0	3000.0
257.	NH2+O2=NH+H02	1.00E+14	0.0	49997.0
258.	NH2+H02=NH3+O2	4.52E+13	0.0	0.0
259.	NH+N0=N2+OH	2.16E+13	-0.2	0.0
260.	NNH+O=N0+NH	1.00E+13	0.0	0.0
261.	NNH+O=N2+OH	1.00E+13	0.0	5000.0
262.	NH2+N0=N2O+H2	5.00E+13	0.0	24481.0
263.	NH+O=N+OH	7.00E+12	0.0	0.0
264.	NH2+O=N0+H2	5.00E+12	0.0	0.0
265.	HCN+O=NC0+H	1.40E+04	2.6	4980.0
266.	HCN+O=CN+OH	2.70E+09	1.6	29200.0
267.	HCN+O=NH+CO	3.50E+03	2.6	4980.0
268.	CN+H2O=HCN+OH	8.00E+12	0.0	7450.0
269.	HCN+OH=HOCN+H	5.90E+04	2.4	12500.0
270.	HCN+OH=HNC0+H	2.00E-03	4.0	1000.0
271.	HCN+OH=NH2+CO	7.80E-04	4.0	4000.0
272.	CN+O2=NC0+O	7.50E+12	0.0	-389.0
273.	NC0+O2=N0+CO2	2.00E+12	0.0	20000.0
274.	HNC0+CN=NC0+HCN	1.50E+13	0.0	0.0
275.	CH4(+M)=CH3(+M)	2.40E+16	0.0	104913.6
	Low pressure limit:	0.45000E+18	0.00000E+00	0.90806E+05
	TR0E centering:	0.10000E+01	0.10000E+03	0.13500E+04 0.78300E+04
276.	CH3NH+OH=CH2NH+H2O	1.00E+08	2.0	0.0
277.	CH3NH+O=CH2NH+OH	1.00E+08	2.0	0.0
278.	CH3NH+O2=CH2NH+H02	1.00E+07	2.0	6300.0
279.	CH3NH+O=CH3O+NH	6.00E+13	0.0	0.0
280.	CH3NH+OH=CH4+HNO	6.00E+12	0.0	0.0
281.	CH3NH+O2=CH3O+HNO	6.00E+12	0.0	4000.0
282.	CH2NH+O=CH2O+NH	1.00E+07	2.0	2800.0
283.	CH2NH+OH=CH2O+NH2	1.80E+05	2.0	14800.0
284.	CH2NH+O=H2CN+OH	3.16E+08	2.0	6100.0
285.	H2CN+H02=CH2NH+O2	7.87E+04	2.0	21700.0
286.	CH2NH+OH=H2CN+H2O	1.00E+07	2.0	4000.0
287.	H2CN+O=HCN+OH	1.00E+07	2.0	6100.0
288.	H2CN+OH=HCN+H2O	1.00E+07	2.0	3700.0
289.	H2CN+O2=HCN+H02	2.70E+04	2.0	17300.0
290.	H2CN+N0=HCN+HNO	1.00E+07	2.0	4400.0
291.	CH3+CH3(+M)=C2H6(+M)	3.61E+13	0.0	0.0
	Low pressure limit:	0.12600E+42	-0.70000E+01	0.27619E+04
	TR0E centering:	0.62000E+00	0.73000E+02	0.11800E+04
292.	CH2NH+M=HCN+H2+M	1.00E+14	0.0	10000.0
293.	2H+M=H2+M	6.52E+17	-1.0	0.0
294.	2H+H2=H2+H2	9.20E+16	-0.6	0.0
295.	NH+N=N2+H	3.00E+13	0.0	0.0
296.	NH+H=N+H2	1.00E+13	0.0	0.0
297.	NH2+H=NH+H2	6.92E+13	0.0	3648.0

298.	NH3+H=NH2+H2	6.36E+05	2.4	10170.0
299.	NNH=N2+H	1.00E+04	0.0	0.0
300.	NNH+H=N2+H2	1.00E+14	0.0	0.0
301.	NNH+NH2=N2+NH3	5.00E+13	0.0	0.0
302.	NNH+NH=N2+NH2	5.00E+13	0.0	0.0
303.	NH2+NH=N2H2+H	5.00E+13	0.0	0.0
304.	2NH=N2+2H	2.54E+13	0.0	0.0
305.	NH2+N=N2+2H	7.20E+13	0.0	0.0
306.	N2H2+M=NNH+H+M	5.00E+16	0.0	50000.0
307.	N2H2+H=NNH+H2	5.00E+13	0.0	1000.0
308.	N2H2+NH=NNH+NH2	1.00E+13	0.0	1000.0
309.	N2H2+NH2=NH3+NNH	1.00E+13	0.0	1000.0
310.	2NH2=N2H2+H2	5.00E+11	0.0	0.0
311.	CH4+H=CH3+H2	1.30E+04	3.0	8037.0
312.	CH4+CH2T=CH3+CH3	4.30E+12	0.0	10036.0
313.	CH3+M=CH2T+H+M	1.00E+16	0.0	90607.0
314.	CH3+H=CH2S+H2	6.00E+13	0.0	15101.0
315.	CH3+H=CH2T+H2	9.00E+13	0.0	15101.0
316.	CH3+CH3=C2H5+H	3.01E+13	0.0	13512.0
317.	CH2T+H=CH+H2	6.00E+12	0.0	-1788.0
318.	CH2T+CH2T=C2H2+H2	1.20E+14	0.0	795.0
319.	CH2T+CH3=C2H4+H	4.20E+13	0.0	0.0
320.	CH2T+CH=C2H2+H	4.00E+13	0.0	0.0
321.	CH2T+C2H6=CH3+C2H5	6.50E+12	0.0	7910.0
322.	CH2S+N2=CH2T+N2	6.00E+12	0.0	0.0
323.	CH2S+CH4=CH2T+CH4	7.20E+12	0.0	0.0
324.	CH2S+C2H2=CH2T+C2H2	4.80E+13	0.0	0.0
325.	CH2S+C2H4=CH2T+C2H4	1.38E+13	0.0	0.0
326.	CH2S+C2H6=CH2T+C2H6	2.16E+13	0.0	0.0
327.	CH2S+CH4=2CH3	4.00E+13	0.0	0.0
328.	CH2S+C2H6=CH3+C2H5	1.20E+14	0.0	0.0
329.	CH+CH4=C2H4+H	6.00E+13	0.0	0.0
330.	CH+CH3=C2H3+H	3.00E+13	0.0	0.0
331.	C2H6=C2H5+H	2.08E+38	-7.1	106507.0
332.	C2H6+H=C2H5+H2	1.41E+09	1.5	7402.0
333.	C2H6+CH3=C2H5+CH4	3.97E+05	2.5	17684.0
334.	C2H5+H=C2H4+H2	1.25E+14	0.0	8000.0
335.	C2H5+CH3=C2H4+CH4	4.36E-04	5.0	8300.0
336.	C2H5+C2H5=C2H4+C2H6	1.40E+12	0.0	0.0
337.	C2H4+M=C2H2+H2+M	3.00E+17	0.0	79349.0
338.	C2H4+M=C2H3+H+M	2.91E+17	0.0	96558.0
339.	C2H4+H=C2H3+H2	5.40E+14	0.0	14902.0
340.	C2H4+H=C2H5	1.05E+14	-0.5	655.0
341.	C2H4+C2H4=C2H5+C2H3	5.00E+14	0.0	64700.0
342.	C2H4+CH3=C2H3+CH4	4.14E+12	0.0	11127.0
343.	C2H3+H=C2H2+H2	1.20E+13	0.0	0.0
344.	C2H3+CH3=C2H2+CH4	4.36E-04	5.0	8300.0
345.	C2H3+C2H6=C2H4+C2H5	1.50E+13	0.0	10000.0
346.	C2H3+C2H3=C2H2+C2H4	1.08E+13	0.0	0.0
347.	C2H3+CH2T=C2H2+CH3	3.00E+13	0.0	0.0
348.	C2H3+CH=CH2T+C2H2	5.00E+13	0.0	0.0
349.	C2H2+C2H2=C2H3+C2H	9.64E+12	0.0	84448.0
350.	C2H2+H=C2H+H2	6.00E+13	0.0	27818.0
351.	C2H2+CH3=C2H+CH4	1.81E+11	0.0	17287.0
352.	C2H2+M=C2H+H+M	4.20E+16	0.0	107000.0
353.	CH+N2=HCN+N	3.00E+11	0.0	13600.0
354.	CN+N=C+N2	1.80E+14	0.0	0.0
355.	CH2T+N2=HCN+NH	1.00E+13	0.0	74000.0
356.	H2CN+N=N2+CH2T	2.00E+13	0.0	0.0
357.	H2CN+M=HCN+H+M	3.00E+14	0.0	22000.0
358.	CH2T+N=HCN+H	5.00E+13	0.0	0.0
359.	CH+N=CN+H	1.30E+13	0.0	0.0
360.	CH3+N=H2CN+H	3.00E+13	0.0	0.0
361.	C2H3+N=HCN+CH2T	2.00E+13	0.0	0.0
362.	CN+H2=HCN+H	3.60E+08	1.6	3000.0
363.	CN+HCN=C2N2+H	1.50E+07	1.7	1530.0
364.	NH3+HNO3=H2O+NH2NO2	8.00E-01	3.5	43100.0
365.	HN03+OH=H2O+N03	9.00E+10	0.0	0.0

366.	$\text{HNO}_3 + \text{H} = \text{NO}_3 + \text{H}_2$	5.60E+08	1.5	16400.0
367.	$\text{HNO}_3 + \text{O} = \text{OH} + \text{NO}_3$	1.80E+07	0.0	0.0
368.	$\text{HNCO} + \text{N} = \text{NH} + \text{NCO}$	2.32E+19	0.0	52500.0
369.	$\text{HNCO} + \text{NO}_3 = \text{CO}_2 + \text{NO} + \text{HNO}$	1.00E+12	0.0	9996.0
370.	$\text{HNCO} + \text{NO}_2 = \text{CO}_2 + \text{HNNO}$	2.51E+12	0.0	26000.0
371.	$\text{HNCO} + \text{HCO} = \text{CH}_2\text{O} + \text{NCO}$	3.00E+12	0.0	26000.0
372.	$\text{HNCO} + \text{M} = \text{H} + \text{NCO} + \text{M}$	1.00E+17	0.0	112000.0
373.	$\text{NCO} + \text{NCO} = \text{CO} + \text{CO} + \text{N}_2$	1.80E+13	0.0	0.0
374.	$\text{N}_2\text{O} + \text{NCO} = \text{CO} + \text{N}_2 + \text{NO}$	9.00E+13	0.0	27800.0
375.	$\text{CN} + \text{NO}_2 = \text{NO} + \text{NCO}$	2.40E+13	0.0	-370.0
376.	$\text{CN} + \text{NO}_2 = \text{CO} + \text{N}_2\text{O}$	4.28E+12	0.0	0.0
377.	$\text{CN} + \text{NO}_2 = \text{CO}_2 + \text{N}_2$	3.13E+12	0.0	0.0

7.3 Predictions of the kinetics model

The above kinetics model is used here to predict the fate of homogeneously premixed $\text{HNCO}/\text{CO}_2/\text{H}_2\text{O}/\text{N}_2\text{O}/\text{HNO}_3/\text{NO}_2$ gaseous compositions. The proposed model is able to simulate ignition at relatively low temperatures. As shown in Fig. 1, for a mixture at a constant volume and at an initial temperature of 480 K and initial pressure of 1 atm, an ignition delay of 19 s is predicted. Here, ignition is numerically defined as the time delay in the system at which point the temperature profile has reached a value within 90% of the maximum. Typically, detailed chemical kinetics models are validated against measured experimental parameters such as ignition delays, species profiles, and fundamental flame speeds that are obtained under “ideal” laboratory setups with homogeneous mixtures at a known temperature and pressure. However, for hypergolic systems, it is very difficult to determine the precise composition, pressure and temperature of the gas phase in which ignition is observed due to the inherent in-homogeneity of the transiently formed mixtures, and therefore it is not easy to validate the detailed chemical kinetics model under consideration. Even in the case for premixed homogeneous systems, such a validation effort in many circumstances is not trivial.

The present detailed chemical kinetics model to predict ignition delays in ILs is first of its kind. Although the predictions are off by 2 orders in magnitude, the present effort represents

a valuable initial step towards understanding hypergolicity in ILs. It should be noted that the model assumes a homogeneous gas mixture in which ignition occurs isotropically throughout the system, whereas the experimental ignition delays reported by Chambreau and Vaghjiani et al. (2008) are for transiently formed mixtures that are highly turbulent as clearly shown in their high-speed videos of the ignition event which is highly localized. Refinements to the model are to be expected in the forthcoming years as new experimental data becomes available from AFRL, Edwards AFB. Similarly, re-appraisal of the rate constant data and/or addition of other pertinent reaction steps as they become available in the literature will improve the fidelity of the model and enhance its quantitative capabilities.

The detailed chemical kinetics model presented here can also be implemented into a computational code, such as Fluent, which incorporates the physics (fluid dynamics) of hypergolic ignition. However, in its present form, our model probably has too many reactions for its efficient implementation. Therefore, reduction techniques can be used to build reduced chemical kinetics models as discussed below.

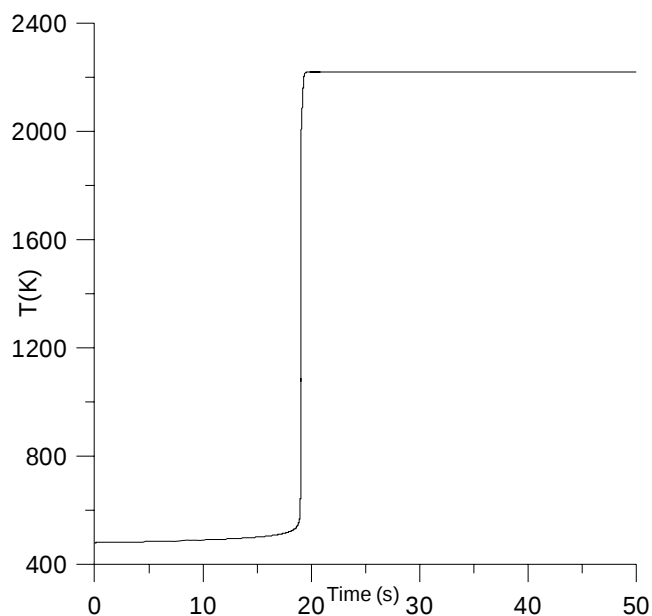


Figure 1. Computed temperature profile against time for a mixture $\text{HNCO}/\text{NO}_2/\text{N}_2\text{O}/\text{CO}_2/\text{H}_2\text{O}/\text{HNO}_3$: 1/1/2/1/1/1. The system is considered to be adiabatic and at constant volume. $P = 1 \text{ atm}$, $T = 480 \text{ K}$, and ignition delay is 19 s.

7.4 Sensitivity analysis

Although it may be premature to perform sensitivity analysis with a non-validated detailed chemical kinetics model, the exercise can allow for the building of a reduced chemical kinetics model. A reduced kinetics model is an abbreviated chemical description of ignition and combustion. There are several approaches for obtaining reduced models through various sensitivity analyses. These analyses allow for the identification of redundant species and reactions, i.e. species and reactions that do not significantly affect the chemical evolution of the system. It is generally recognized that quite often about 90% of the initial reactions in the detailed model can be eliminated (depending on the required conditions of composition, temperature, and pressure) to produce a much smaller and tractable reduced model with fidelity characteristics similar to that of the starting model.

7.4.1 Brute force sensitivity analyses

These analyses can be divided into three groups. One brute force sensitivity analysis involves the running of the model by perturbing one parameter and comparing the results to the predictions of the unperturbed model. For instance, a rate constant can be set equal to zero (as if the considered reaction was removed from the model). Such a sensitivity analysis allows one to determine whether or not the presence of a reaction is important for ignition. Another brute force sensitivity analysis uses multipliers for the pre-exponential factor of a rate constant (generally between two and five). In this case, the sensitivity analysis allows one to assess the effect of the magnitude of the rate constant. Both techniques are simple but quickly become inefficient for large models that contain one hundred or more reactions. Never the less, they are recognized as the most utilized approaches for modeling ignition delay times. A third brute force sensitivity analysis, which is rarely used, requires one to modify the thermodynamics data of key species, according to experimental (or computational) uncertainties. This brute force sensitivity analysis is very cumbersome because of the number of perturbations that are possible (for the standard enthalpy of formation at 298.15 K, C_p° , and S°). As discussed in section 5, we have begun to compile the necessary thermochemical database to enable us to perform such an analysis in the future.

7.4.2 First-order sensitivity analyses

These sensitivity analyses have been developed as alternatives to brute force sensitivity analyses. They directly calculate first-order sensitivity coefficients by taking the derivatives of the governing equations and are particularly suitable for analyzing species profiles.

However, these first-order sensitivity analyses are generally less informative when it comes to predicting ignition delays.

7.4.3 Results

For the composition considered in Fig. 1, the present model suggests that the presence of NO₂ in the system has a significant effect on the predicted value of the ignition delay. With a smaller amount of NO₂, an ignition event is still simulated as shown in Fig. 2 but with a longer ignition delay (by a factor of about 3). The question as to whether or not NO₂ is indispensable for ignition arises. Fig. 3 shows that ignition is possible even if no NO₂ is initially present. However, under this situation the ignition delay is an order of magnitude longer. It therefore appears that in this model, even a small amount of NO₂ promotes ignition. The present brute force sensitivity analyses suggest that the initiation reaction, $\text{HNO}_3 \rightarrow \text{OH} + \text{NO}_2$, may be an important process to consider in the construction of a reduced chemical kinetic model.

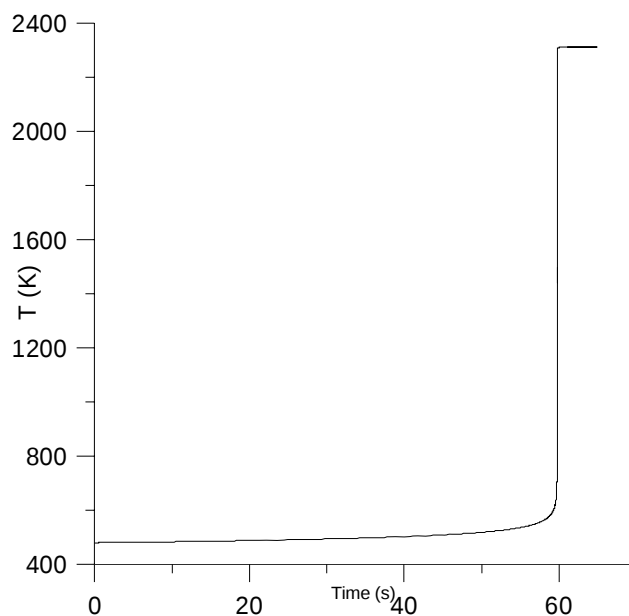


Figure 2. Computed temperature profile against time for a mixture HNCO/NO₂/N₂O/CO₂/H₂O/HNO₃: 1/0.01/2/1/1/1. The system is adiabatic and at constant volume. P = 1 atm, T = 480 K, ignition delay is 59 s.

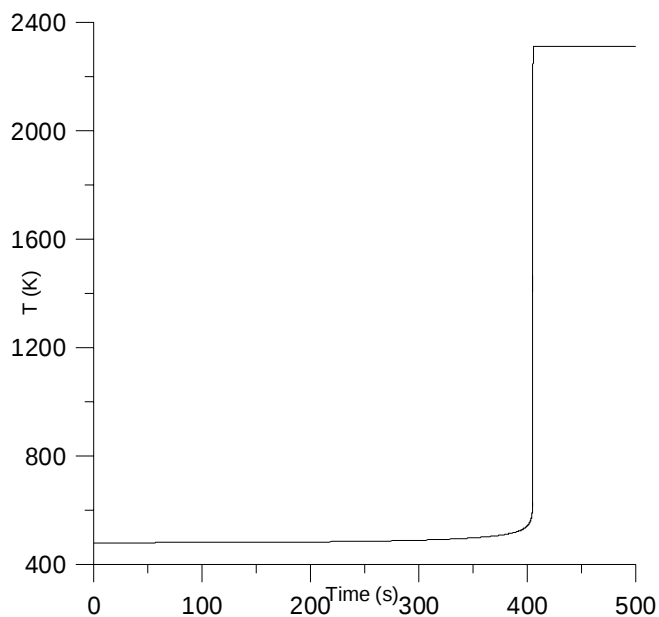


Figure 3. Computed temperature profile against time for a mixture HNCO/NO₂/N₂O/CO₂/H₂O/HNO₃: 1/0/2/1/1/1. No NO₂ is present initially. The system is adiabatic and at constant volume. P = 1 atm, T = 480 K, ignition delay is about 400 s.

8. Conclusion and perspective

Thermochemical calculations at equilibrium show that species observed in the gas phase above the liquids are able to sustain a flame, and that many of the important species needed to explain hypergolic ignition have probably been identified. The present calculations also show that the thermal decomposition of isocyanic acid (HNCO) is exothermic. Even if pure HNCO decomposition cannot sustain a flame, the exothermicity of the process most likely plays an important role in defining the ignition characteristics of the system.

A detailed chemical kinetics model has been proposed to explain hypergolic ignition in ionic liquid-based systems. The model is able to simulate ignition at relatively low initial temperatures. Although initial gas phase presence of NO_2 is not needed to explain hypergolic ignition, the model shows that its presence can significantly affect the computed ignition delay values, and that introduction of a very small amount of NO_2 in the model can profoundly reduce the calculated delay times.

A quantitative assessment of the predictions from the detailed chemical kinetic model and experimental values is not possible at this time since calculations are done by considering a static adiabatic reactor filled with a homogeneous premixed gas composition at a given initial pressure and initial temperature. In this ideal reactor, diffusion of species and thermal transfer (by conduction and convection) is ignored. Whereas in the real experimental reactor, reactive species are formed in the liquid phase and indeed diffuse from the hot liquid surface to the gas phase. Therefore, gradients of composition, temperature and pressure exist in the whole volume above the liquid surface, and the measured ignition delay will have contributions from both the time to diffuse (physical delay) and the time to react (chemical delay). Hence

consideration of chemistry alone in a numerical model will not explain quantitatively all of the experimental observations. A numerical code that also includes diffusion of species, fluid mechanics and thermal transfer processes will be needed to accomplish this. The detailed chemical kinetic model presented in this report is probably too big for its implementation into such a physical code and therefore the construction of a reduced kinetics model will be required first. A complete sensitivity analysis on this reduced model will then be needed to ascertain the role of various oxidants such as OH, O, NO₂, and N₂O, etc. in the system. Finally, a validation effort will be needed to optimize the reduced kinetics model.

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