A Thermodynamic Properties Estimation Method
for Isocyanates

Will Meyerriecks

702 Leisure Avenue, Tampa, FL 33613, USA

ABSTRACT

The accurate estimation of the adiabatic flame temperature is necessary when evaluating a composite propellant. This in turn requires additional formulation and properties data including the reactant percentages, chemical formulas, and formation enthalpies, where the latter is sometimes difficult to obtain. When experimental data is not available, one must use estimation methods. The estimation method or its software implementation may not completely describe all components or properties of interest, however. This is often the case with isocyanates. The author has assembled thermodynamic data for a variety of isocyanates and, from this, has derived Benson Group values that may be used in estimating isocyanate properties when experimental data is unavailable. Application of these estimates and their effect on the estimation of the adiabatic flame temperature is considered.

Keywords: isocyanate, diisocyanate, urethane, enthalpy of formation, Benson group, estimation, adiabatic flame temperature

Introduction

There are many properties of a composite propellant that are of interest to the energetics chemist. These include, but are not limited to, the chemical formulation, adiabatic flame temperature, and the resulting products gas composition and properties as a function of pressure. Generally, the chemical composition of the propellant ingredients is well established. What is sometimes unknown is the formation enthalpy ($\Delta_f H°$) of a particular ingredient. This property represents the energy required to form this molecule from its constituent elements in their standard states.[1] When the combustion reaction takes place, and one assumes an adiabatic condition, where no heat is gained or lost in the system,[2a] the enthalpy of the products equals that of the reactants. This is the adiabatic, or maximum theoretical, flame temperature. Thus, knowledge of the reactant formation enthalpies is required to accurately estimate the flame temperature and combustion properties at this temperature.

Many composite propellants utilize polymers to bind together the oxidizer and metal fuel particles, and these polymers contribute to the combustion process as a fuel source. Polyurethanes are frequently used in this capacity due to their relatively low cost, high performance, and rheological properties. A polyurethane, put quite simply, is a thermoplastic polymer produced by the condensation reaction of an isocyanate and a hydroxyl-containing material.[2b] An isocyanate (NCO) is a nitrogen, carbon, and oxygen double bonded together, and this functional group is bonded to a "base" molecule.[2c] A hydroxyl (OH) is a hydrogen bonded to an oxygen, which is in turn bonded to a "base" molecule.[2d] See Figure 1.

A common propellant binder composition includes the long chain hydrocarbon HTPB (hydroxyl-terminated polybutadiene) and the diisocyanate IPDI (isophorone diisocyanate). The diisocyanate differs from the isocyanate in that each molecule contains two of the isocyanate functional groups. Examples of both iso- and diisocyanates are in Figure 2 (located after references). HTPB (see Figure 3) has a hydroxyl (OH) group at both ends of the molecule, and IPDI has two isocyanate groups (NCO). In the process of reaction, the HTPB and IPDI form a urethane bond (see Figure 1) that unites them, and a synthetic rubber results.
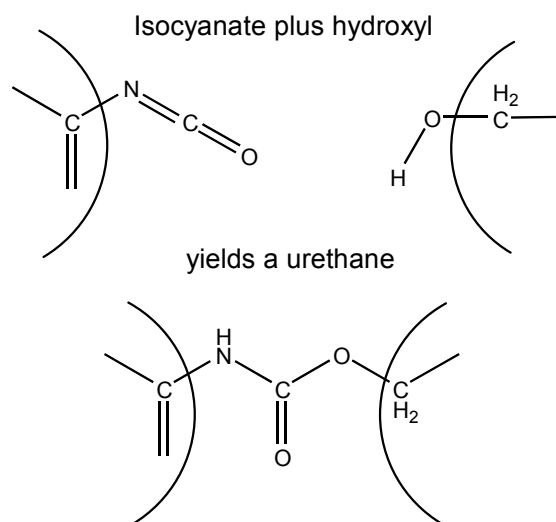
Isocyanate plus hydroxyl

yields a urethane

Figure 1. Urethane bond between an isocyanate and a hydroxyl.

Data

For many isocyanates there is little thermodynamic data available despite the use of these chemicals in tremendous quantities in the plastics and coatings industries. The urethane condensation reaction mechanism is poorly understood,[3] and the availability of critically evaluated experimental data is in short supply.[4]

A search for thermodynamic data can sometimes be a lesson in frustration. What is available at a conventional library is minimal at best, difficult to locate, and often disappointing in scope. Fortunately, there are sources of data that are readily available—ones that provided most of the data presented here.

In particular is an Internet web site maintained by the National Institute of Standards and Technology (NIST), *NIST Chemistry WebBook.*[5] This online database includes thermodynamic data for many molecules, of which a few are iso- and diisocyanates. As of this writing, the ability to search for specific compounds is limited to full chemical names, Chemical Abstract Registry (CAS) numbers, and partial formulas.

Another web site, CambridgeSoft's *ChemFinder,*[6] has a large database of organic molecules, and this search engine allows partial name searches. When "isocyanate" is used as a partial name search, up to 25 "hits" are displayed. Selecting any of these items displays the chemical structure (if known), formula, CAS registry number, and other properties information. This proved useful in determining the CAS numbers for particular isocyanates. The NIST site was then used to cross reference the thermodynamic properties when they were available. In addition, the structural drawing found on *ChemFinder* proves valuable too, as described later. The 25 hits limit of the *ChemFinder* web site was eliminated by use of *ChemOffice Ultra,*[7] which includes the complete database found on the web site.

The data and sources are listed in Appendix 1. All data presented is referenced at 298.15 K. Temperatures are in Kelvin. Units are kJ/mol for $\Delta_f H^\circ$ (enthalpy), and J/(mol·K) for C_p° (heat ca-
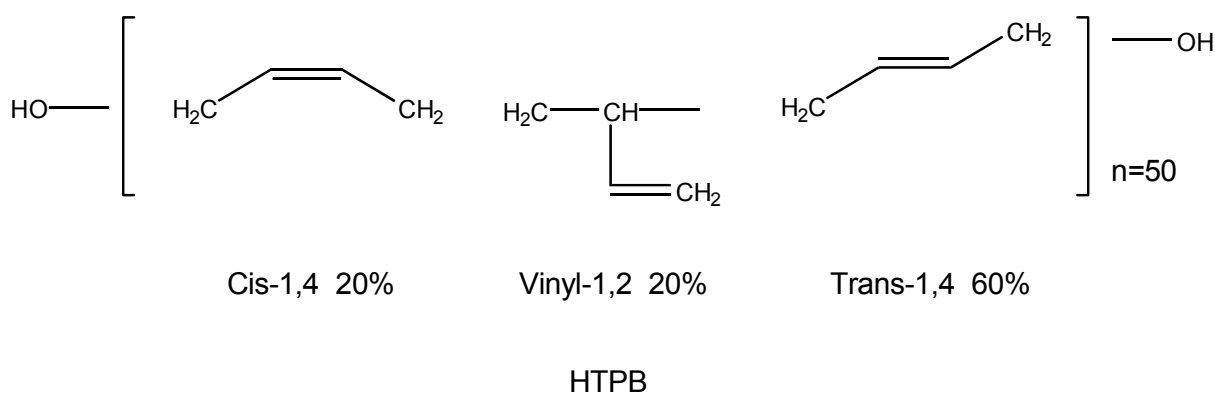

HTPB

Figure 3. HTPB (hydroxyl terminated polybutadiene).[22]

pacity) and S^o (entropy). In the gas phase, only Δ_fH^o was found; some of these values are estimates as noted in the data. In the liquid and solid phases, only Δ_fH^o and C_p^o were found with three exceptions for S^o. Some of the data was contradictory or apparently erroneous and is so noted. Of primary importance in estimating the adiabatic flame temperature is the liquid phase Δ_fH^o; the isocyanates and hydroxyl-terminated polymers used in propellants are liquids and react to form a viscoelastic fluid as opposed to a crystalline solid. The majority of the Δ_fH^o data found is for the solid phase.

The Benson Group Additivity Method

Where experimental data does not exist, one must estimate the required properties. There are a variety of methods available for the gas phase. The interested reader is directed to reference 8 for lucid descriptions and sample calculations of five methods, including that of Benson. For composite solid propellant evaluation, the liquid phase is generally of most interest. The method of Benson has been extended to the liquid and solid phases by Domalski and Hearing,[9] and is available from NIST as the software database program *THERM*.[10] This program was used extensively in evaluating the thermodynamic data presented herein.

The Benson Group method assigns thermodynamic values to specific groupings of atoms that are commonly found in organic molecules containing the elements C, H, N, O, S, Cl, Br, I, and F, for which a large body of experimental thermodynamic data is available. Specifically, the molecule is broken down into groups where each group is generally the non-hydrogen atom of interest and the atoms immediately bonded to it. For example, methane, CH_4, is a carbon atom with 4 hydrogens bonded to it. In Benson Group notation, this is equivalent to C–$(H)_4$. Methanol, CH_3OH, has 2 groups: a carbon bonded to 3 hydrogens and an oxygen, C–$(H)_3(O)$, and an oxygen bonded to a carbon and a hydrogen, O–(H)(C). Carbons that have single, double, triple, and resonant bonds are given the notations C, C_D, C_T, and C_B, respectively. Unsubstituted benzene, for example, would be six C_B–$(H)(C_B)_2$ groups. There are corrections for a variety of molecular configurations. Hexane,

C_6H_{12}, when formed into the ring structure cyclohexane, imparts additional strain on the carbon bonds. The notation used is still six C–$(H)_2(C)_2$ groups, but then a "correction" group "Cyclohexane, RSC" is included to account for this strain. When substitutions are made on a "base" structure, their proximity to other groups can impart additional strain. Examples of this include methyl substitution (a "–CH_3 correction"), and the neighboring interaction ortho and meta substitutions, such as *o*-xylene and *m*-xylene.[10a]

After all of the component groups are identified, their respective contributions are arithmetically summed, corrections are applied when required, and the resulting values are the estimates of the thermodynamic properties. This method and its extension to liquid and solid phases is surprisingly accurate despite its apparent simplicity.[9] The primary problem in evaluating the properties of isocyanates using this method is that no values for the NCO group have yet been defined[9] due to the lack of critically evaluated data.[4]

NCO Group Estimation

The NCO group contributions are required to complete the estimation of the isocyanate properties. Based on the chemical structures for which thermodynamic data was available (see Figure 2) only three variations of the NCO group are considered based on the specific type of carbon-nitrogen bond: a carbon, C, a resonant carbon C_B, and a doubly bonded carbon C_D. The group notations used for these three cases are N–(C)($_DCO$), N–(C_B)($_DCO$), and N–(C_D)($_DCO$). The introduction of the ($_DCO$) nomenclature is to suggest that the CO group is itself double bonded to the nitrogen via the carbon rather than using the notation $(CO)_2$ which indicates that two separate CO groups bond to the nitrogen. This was also adopted so as not to create confusion with the N_A and N_I nomenclature used for azo and imino nitrogen bonding.

Estimating the properties of the NCO group is straightforward: using a structural diagram of the molecule, like that found on the *Chem-Finder* database, sum the respective contributions of all of the other (known) groups in the molecule, and then subtract this sum from the

cited value. The contribution of the NCO group is the remainder. In the case of the molecule being a diisocyanate, the remainder is divided by two, half for each contributing NCO group. Diisocyanates such as IPDI were not used in estimating the NCO group values due to the molecule having multiple C–NCO bond types. The tabulated results are presented in Table 1 (located after references) and are organized by phase—gas, liquid, and solid, and by property type—formation enthalpy ($\Delta_f H^o$), heat capacity (C_p^o), and entropy (S^o). Arithmetic averages appear for the various properties and bond types. Due to the limited number of data points available, no statistical methods were applied to the data. One value, as noted, was excluded due to its inconsistent and possibly inaccurate value. Appendix 2 outlines a brief study of para, meta, and ortho group substitutions effects.

Urethane Reaction Estimate

One may wish to consider the reaction between the component isocyanate and hydroxyl compounds that result in a urethane. There are no values for the CO–(O)(N) group, however.[9,10] The gas and liquid phase $\Delta_f H^o$ contributions for this group were estimated from the two urethanes listed in Table 2. Due to this very sparse data, and for the sake of completeness, the author used a different approach to "fill in the gap" for the solid phase $\Delta_f H^o$, as detailed in Table 2. The differences between these single-atom estimates and those estimated from the two urethanes were 0.82 kJ/mol$_{gas}$ and –9.33 kJ/mol$_{liquid}$ for $\Delta_f H^o$. This agreement lends confidence to the solid phase $\Delta_f H^o$ estimate. These are all tentative figures, nonetheless, and should be treated as such.

As an example of this reaction, when a mole of HTPB and a mole of IPDI completely react, the resulting urethane $\Delta_f H^o$ does not equal that of the reactants due to the rearrangement of the atoms taking place in the urethane bond. For this particular case, and using the $\Delta_f H^o$ values in Table 3 combined with the estimated CO–(O)(N) group value and bond rearrangements, the resulting rubber has a $\Delta_f H^o$ of –230.63 kJ/mol$_{liquid}$ as compared to the combined reactants respective $\Delta_f H^o$ of 17.65 kJ/mol$_{liquid}$—a

heat of reaction[2e] of –248.28 kJ/mol$_{liquid}$. This difference represents two moles of urethane bonds due to the reactants having a functionality of two. Thus, the estimated, exothermic heat of reaction per mole of urethane bonds, in this case, is –124.14 kJ/mol$_{liquid}$.

Application of Results

From these tabulated values, one can estimate the properties for other isocyanates. As an example, estimates for IPDI agree reasonably well with reference 16 rather than reference 19 or 21. Appendix 3 compares a sample of estimated isocyanate enthalpies to values used in the propulsion industry. There are significant differences in some cases. This leads one to consider how the isocyanate $\Delta_f H^o$ estimate impacts the prediction of the adiabatic flame temperature of a composite propellant.

To evaluate this, simulations were run using the author's free energy minimization program.[11] Each simulation was run six times: once each for the two cited values for IPDI, and once each for the as-estimated $\Delta_f H^o$ value, this value divided by two, this value multiplied by two, and for the urethane system described above that represents the cured (reacted) isocyanate and hydroxyl-terminated polymer.

Two generic propellants were used in this evaluation, and their formulations and test results are presented in Table 3. The diisocyanate contributes only a small percentage to the mass of the propellant, and thus its overall contribution to the propellant enthalpy is minor. Even so, the intentionally poor $\Delta_f H^o$ estimates (times 2, divided by 2) indicate that there is a subtle, but definite, effect on the flame temperature. Although it is a small variation, it should not be ignored. Accounting for the urethane reaction enthalpy resulted in a change to the estimated flame temperature that is almost as significant as that of the intentional errors in the isocyanate enthalpy for these particular formulations.

Conclusion

Experimental thermodynamic data for isocyanates may be hard to find, but with the data that is available, reasonable NCO group values may be estimated. These Benson Group NCO values accommodate the estimation of some of the thermodynamic properties of the arbitrary isocyanate, which may then be considered in evaluating the composite propellant as a whole. The overall effect of the isocyanate enthalpy on the adiabatic flame temperature is minimal; even so, every effort should be made to acquire or estimate accurate $\Delta_f H^o$ values, especially in situations where the effective enthalpy contribution is greater. The effect of the urethane reaction should not be overlooked or ignored either, as it is relatively easy to estimate and account for using similar group additivity methods.

References

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11) Will Meyerriecks, *CEQ Chemical Equilibrium*, Version 36E.

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Notes on References

Data for references 16 and 21 is in an unusual format that seems to be prevalent in the propulsion industry: enthalpy values are expressed in kCal/100 g, and it is rounded to integer values in reference 21. The appropriate steps were made to convert to the molecular weight of the molecule and then to kJ/mol. None of this data was used in the estimates as the original sources of these values are unknown, and sometimes the phase was unknown as indicated. (Estimates based on the methods outlined were used to compare against some of these compounds for illustrative purposes. See Appendix 3.)

Figure 2. Isocyanate and urethane molecular structures.

1   Benzene, 1,1'-methylenebis[4-isocyanato- 101-68-8

2   Benzene, 1,2-dichloro-4-isocyanato- 102-36-3

3   Benzene, isocyanato- 103-71-9

4   Benzene, 1-chloro-4-isocyanato- 104-12-1

5   Benzene, 1,4-diisocyanato- 104-49-4

6   Ethane, isocyanato- 109-90-0

7   Benzene, 1-isocyanato- 111-36-4

8   Octadecane, 1-isocyanato- 112-96-9

9   2,4,4Trimethylhexamethylene diisocyanate 15646-96-5

10   Toluene diisocyanate 26471-62-5

11   4,4'-Biphenyldiisocyanate 2761-22-0

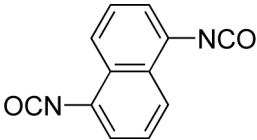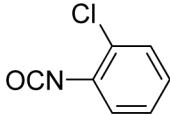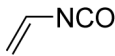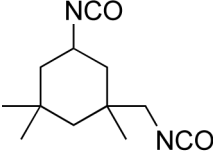12   Benzene, 1-chloro-3-isocyanato- 2909-38-8

Figure 2. Continued.
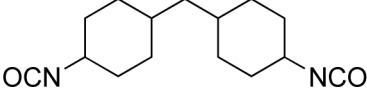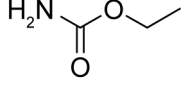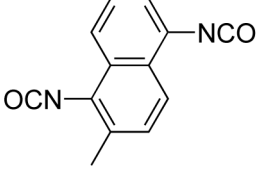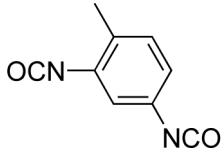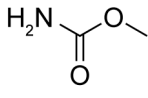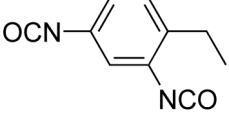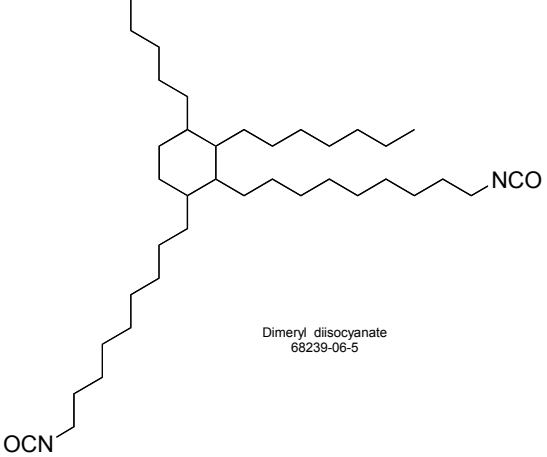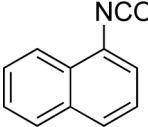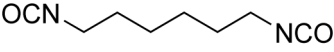
13 Naphthalene, 1,5-diisocyanato- 3173-72-6	**14** Benzene, 1-chloro-2-isocyanato- 3320-83-0	**15** Ethene, isocyanato- 3555-94-0
16 Isophorone Diisocyanate 4098-71-9	**17** Cyclohexane, 1,1'-methylenebis[4-isocyanato- 5124-30-1	**18** Urethane 51-79-6
19 2-Methyl-1,5-naphthalene diisocyanate 56775-58-7	**20** Benzene, 2,4-diisocyanato-1-methyl- 584-84-9	**21** Carbamic acid, methyl ester 598-55-0

22 Methane, isocyanato- 624-83-9	**23** Ethyl-m-phenylene diisocyanate 64711-83-7	**24** Dimeryl diisocyanate 68239-06-5

Dimeryl diisocyanate
68239-06-5

25 Naphthalene, 1-isocyanato- 86-84-0	**26** 1,6-Hexamethylene diisocyanate 822-06-0

Table 1. NCO Benson Group Contribution Estimates.

N–(C_B)(_DCO)

Fig. 2 Diag. No.	CAS #	Gas ΔfH°	Liquid ΔfH°	Liquid Cp°	Liquid S°	Solid ΔfH°	Solid Cp°	Solid S°
25	86–84–0					–57.66		
1	101–68–8	40.14[a]	–53.0			–65.55	48.71	106.90
						–66.85		106.90
						–65.45		
2	102–36–3					–92.84		
3	103–71–9	–57.75[b]	–76.2	57.78				
4	104–12–1					–87.57	83.83	
5	104–49–4						52.59	
20	584–84–9			88.06				
11	2761–22–0					–78.00		
12	2909–38–8			45.99		–88.67		
13	3173–72–6						36.11	
14	3320–83–0					–83.37		
19	56775–58–7					–91.59		
23	64711–83–7	–67.25	–86.74					
	Average:	–62.50	–71.98	63.94	N/A	–77.76	55.31	106.90

Units   ΔfH°   kJ/mol
            Cp°   kJ/(mol•K)
            S°   kJ/(mol•K)

N–(C)(_DCO)

Fig. 2 Diag. No.	CAS #	Gas ΔfH°	Liquid ΔfH°	Liquid Cp°	Liquid S°	Solid ΔfH°	Solid Cp°	Solid S°
6	109–90–0	–79.94[b]	–39.61					
7	111–36–4	–88.18[b]						
8	112–96–9					–67.10		
22	624–83–9	–87.74	–44.39					
			–42.37					
26	822–06–0			55.74	112.91		45.99[c]	51.97[c]
17	5124–30–1	–44.41				–78.38		
	Average:	–75.07	–42.12	55.74	112.91	–72.74	45.99	51.97

N–(C_D)(_DCO)

Fig. 2 Diag. No.	CAS #	Gas ΔfH°	Liquid ΔfH°	Liquid Cp°	Liquid S°	Solid ΔfH°	Solid Cp°	Solid S°
15	3555–94–0	–40.32[b]	N/A	N/A	N/A	N/A	N/A	N/A

[a] Value is possibly not accurate and has been excluded from the average.

[b] These gas phase enthalpies are based on estimates.

[c] CAS 28182–81–2, 1,6-Hexamethylene diisocyanate $C_8H_{12}N_2O_2$.

Table 2. CO–(O)(N) – Group Estimates.

Estimated Values for the Group CO–(O)(N) Experimental Data

Fig. 2 Diag. No.	CAS #	Gas ($\Delta_f H°$)	Liquid ($\Delta_f H°$)	Solid ($C_p°$)
18	51–79–6	–446.30	–497.30	156.43
21	598–55–0	–425.30	–472.70	N/A

The resulting CO–(O)(N) contribution:

CAS #	Gas ($\Delta_f H°$)	Liquid ($\Delta_f H°$)	Solid ($C_p°$)
51–79–6	–119.27	–153.97	88.56
598–55–0	–131.17	–165.17	N/A
Average:	**–125.22**	**–159.57**	**88.56**

Known Benson Group/Single-Atom Contribution Estimates

The following *THERM* Groups were used to derive the average contribution of a single-atom to a CO (carboxyl) group for $\Delta_f H°$:

CAS #	Gas ($\Delta_f H°$)	Liquid ($\Delta_f H°$)	Solid ($\Delta_f H°$)
Group 121, CO–(C)$_2$	–132.67	–152.76	–157.95
Group 116, CO–(O)$_2$	–111.88	–122.00	–123.00
Group 289, CO–(N)$_2$	–111.00	–190.50	–203.10

Dividing each of the above by 2 gives the single-atom contribution. Adding these single-atom values, then subtracting this from the known value for the actual group gives the methods residual error:

CAS #	Gas ($\Delta_f H°$)	Liquid ($\Delta_f H°$)	Solid ($\Delta_f H°$)
Group 114, CO–(C)(O)	–137.24	–149.37	–153.60
Single-atom contributions	–122.28	–137.38	–140.48
error	– 14.96	– 11.99	– 13.12
Group 239, CO–(C)(N)	–133.26	–185.00	–194.60
Single-atom contributions	–121.34	–171.63	–180.53
error	– 11.92	– 13.37	– 14.07
Average error:	– 13.44	– 12.68	– 13.60

The error is evenly distributed, and for all phases it is –13.24.

The atoms are added together, and the average error added to that sum to yield values for an **estimated Group CO–(O)(N) $\Delta_f H°$**:

CAS #	Gas ($\Delta_f H°$)	Liquid ($\Delta_f H°$)	Solid ($\Delta_f H°$)
O and N contributions	–110.94	–156.25	–163.05
error contribution	– 13.44	– 12.68	– 13.60
CO–(O)(N) Group $\Delta_f H°$:	**–124.4**	**–168.9**	**–176.7**

Table 3. Isocyanate $\Delta_f H^o$ Estimate Effect on Adiabatic Flame Temperature.

Application of NCO Group Estimates

Propellant Ingredients

Ingredient	Formula	mw	$\Delta_f H^o$
HTPB	$C_{200}H_{302}O_2$	2738.60	365.22 kJ/mol[a]
IPDI	$C_{12}H_{18}N_2O_2$	222.29	variable
Ammonium Perchlorate	NH_4ClO_4	117.49	−295.3[b]
Aluminum	Al	26.98	0

Propellant Compositions

Ingredient	Propellant One	Propellant Two
Ammonium Perchlorate	70.0 %	80.0%
Aluminum	15.0%	0.0%
HTPB[c]	13.875%	18.5%
IPDI[c]	1.125%	1.5%

Flame Temperature, K[d]

IPDI $\Delta_f H^o$	Source	One	Two
−371.62	Ref. 16	3280.6	2363.3
−466.21	Ref. 19, 21	3279.2	2360.5
−347.57	Estimate	3280.6	2363.3
−347.57	Urethane[e]	3277.8	2354.9
−695.14	Estimate *2	3275.1	2352.1
−173.79	Estimate / 2	3284.8	2370.2

[a] Value estimated by the author using NIST *THERM* (reference 10), based on structure in reference 22. See Figure 3.

[b] Value from reference 18b.

[c] In both propellants, the NCO:OH ratio is 1:1.

[d] Flame temperature is estimated using reference 11 and convergence is computed using a binary subdivision between 298.15 K and 6000 K, until the difference between successive iterations is less than 1.0 degree K as the reactant minus product enthalpies approaches zero.

[e] The *urethane* is equivalent to the estimated HTPB and IPDI reacting to form a urethane, and the resulting product estimate includes the CO–(O)(N) estimated $\Delta_f H^o$. The value used in the simulation for the resulting product has the formula $C_{212}H_{320}N_2O_4$, molecular weight 2960.88, and $\Delta_f H^o$ of −230.63 kJ/mol.

Appendix 1

CAS Number	Phase	Property	Value	Ref.	Comments
86–84–0	Naphthalene, 1-isocyanato-				
	Solid	$\Delta_f H° =$	26	15	
101–68–8	Benzene, 1,1'-methylenebis [4-isocyanato-				
	Gas	$\Delta_f H° =$	189 (+/–21)	15	** Questionable accuracy
	Liquid	$\Delta_f H° =$	–25.5	17	
	Solid	$\Delta_f H° =$	–53.0	15	
			–55.6	15	
			–52.8	17	
		$C_p° =$	307.0	15	
		$S° =$	332.5	15	
			332.5	15	
102–36–3	Benzene, 1,2-dichloro-4-isocyanato-				
	Solid	$\Delta_f H° =$	–119	15	
103–71–9	Benzene, isocyanato-				
	Gas	$\Delta_f H° =$	10	15	Estimate
	Liquid	$\Delta_f H° =$	33.9	15	** Typographical error?
			–33.9	15	
		$C_p° =$	186.2	15	
104–12–1	Benzene, 1-chloro-4-isocyanato-				
	Solid	$\Delta_f H° =$	–83.7	15	
		$C_p° =$	210.9	15	
104–49–4	Benzene, 1,4-diisocyanato-				
	Solid	$C_p° =$	211.7	15	
109–90–0	Ethane, isocyanato-				
	Gas	$\Delta_f H° =$	–150	15	Estimate
	Liquid	$\Delta_f H° =$	–118.02	20	
111–36–4	Butane, 1-isocyanato-				
	Gas	$\Delta_f H° =$	–200	15	Estimate
112–96–9	Octadecane, 1-isocyanato-				
	Solid	$\Delta_f H° =$	–618.4	15	
584–84–9	Benzene, 2,4-diisocyanato-1-methyl-				
	Liquid	$C_p° =$	287.8	15	
624–83–9	Methane, isocyanato-				
	Gas	$\Delta_f H° =$	–130	15	
	Liquid	$\Delta_f H° =$	–92.0	18a	

CAS Number	Phase	Property	Value	Ref.	Comments
822–06–0	1,6-Hexamethylene diisocyanate				
	Liquid	C_p° =	294.0	15	
		S° =	420.1	15	
	Solid	C_p° =	45.59	15	** 28182–81–2
		S° =	51.97	15	** 28182–81–2
		$\Delta_f H^\circ$ =	−226.18	16	** Phase unknown
		$\Delta_f H^\circ$ =	−504.70	21	** Phase unknown
2761–22–0	4,4'-Biphenyldiisocyanate				
	Solid	$\Delta_f H^\circ$ =	−50.2	15	
2909–38–8	Benzene, 1-chloro-3-isocyanato-				
	Liquid	C_p° =	187.0	15	
	Solid	$\Delta_f H^\circ$ =	−82.80	15	
3173–72–6	Naphthalene, 1,5-isocyanato-				
	Solid	C_p° =	223.6	15	
3320–83–0	Benzene, 1-chloro-2-isocyanato-				
	Solid	$\Delta_f H^\circ$ =	−74.50	15	
3555–94–0	Ethene, isocyanato-				
	Gas	$\Delta_f H^\circ$ =	−30	15	Estimate
4098–71–9	Isophorone diisocyanate				
	Liquid	$\Delta_f H^\circ$ =	−466.21	19	
			−466.07	21	
			−371.62	16	
5124–30–1	Cyclohexane, 1,1'-methylenebis[4-isocyanato-				
	Gas	$\Delta_f H^\circ$ =	−311 (+/− 12)	15	
	Solid	$\Delta_f H^\circ$ =	−440.6	15	
15646–96–5	2,4,4-Trimethylhexamethylene diisocyanate				
		$\Delta_f H^\circ$ =	−377.61	16	** Phase unknown
26471–62–5	Toluene diisocyanate, see 584-84-9				
		$\Delta_f H^\circ$ =	−24.05	16	** Phase unknown
		$\Delta_f H^\circ$ =	−623.17	21	** Phase unknown
56775–58–7	2-Methyl-1,5-naphthalene diisocyanate				
	Solid	$\Delta_f H^\circ$ =	−133	15	
64711–83–7	Ethyl-*m*-phenylenediisocyanate				
	Gas	$\Delta_f H^\circ$ =	−135	15	Mixture
	Liquid	$\Delta_f H^\circ$ =	−196	15	Mixture
68239–06–5	Dimeryl diisocyanate				
		$\Delta_f H^\circ$ =	−1236.33	16	** Phase unknown
		$\Delta_f H^\circ$ =	−872.60	21	** Phase unknown

Appendix 2

The groups used in estimating the NCO contributions included corrections where required, such as ortho Cl–Cl, meta, CH_3 tertiary and quaternary substitutions, etc. The available experimental data is too limited to draw any conclusions in terms of the development of additional correction groups for NCO–NCO, CH_3–NCO, and Cl–NCO next-to-nearest neighbor interactions. Nonetheless, *MOPAC* [12] was used to investigate these interactions. The method used was to draw the structure in *ChemDraw Pro*, [13] import it into *Chem 3D Pro*, [14] and then minimize the strain of the structure using the PM3 Hamiltonian.

The two structures studied were benzene and the *chair* conformation of cyclohexane. An NCO group was substituted, and a second group X was substituted in the para, meta, or ortho position relative to the first group. This second group X was either CH_3, Cl, or NCO. The results are tabulated below in both $\Delta_f H^o{}_{gas}$ and the difference between the para value and that of the current position. The interaction did not become really significant until the ortho position, and in most of the available data, this condition does not arise.

The exception to this, for which $\Delta_f H^o{}_{gas}$ is available, is a meta NCO–NCO interaction, 64711–83–7, ethyl-*m*-phenylenediisocyanate. The cited $\Delta_f H^o{}_{gas}$ is –135 kJ/mole. The *MOPAC* estimate is –47.18. This represents a significant difference that cannot be easily evaluated without additional gas phase enthalpy data.

Benzene

Position	CH_3	Cl	NCO	ΔCH_3	ΔCl	ΔNCO
para	9.86	21.66	1.95	0	0	0
meta	9.97	21.89	1.35	0.11	0.23	–0.6
ortho	18.49	25.83	11.82	8.63	4.17	9.87

Cyclohexane

Position	CH_3	Cl	NCO	ΔCH_3	ΔCl	ΔNCO
para	–185.04	–182.75	–187.89	0	0	0
meta	–184.96	–182.43	–192.84	0.08	0.32	–4.95
ortho	–174.72	–177.42	–180.33	10.32	5.33	7.56

Appendix 3

Comparison of Estimated and Cited Isocyanate Enthalpies

Fig. 2 Diag. No.	Estimated $\Delta_f H^o$			Cited $\Delta_f H^o$	Ref
	Gas	Liquid	Solid		
26	822-06-0	1,6-Hexamethylene diisocyanate			
	–289.26	–248.76	–331.12	–226.18	16
				–504.70	21
16	4098–71–9	Isophorone diisocyanate			
	–335.15	–347.57	–398.33	–371.62	16
				–466.21	19
				–466.07	21
9	15646–96–5	2,4,4 Trimethylhexamethylene diisocyanate			
	–362.15	–332.22	–414.13	–377.61	16
10	26471–62–5, Toluene diisocyanate				
	–104.16	–141.67	–142.27	–24.05	16
				–623.17	21
24	68239–06–5	Dimeryl diisocyanate			
	–871.45	–972.86	–1125.06	–1236.33	16
				–872.60	21

1) The phase of the cited values listed is unknown.

2) The chemical name of the cited value, and its value, were all that was available for the above. It is assumed to be the same as those presented by CAS registry number.

Appendix 4

Suggested Values for the NIST THERM Database file THERM.COD

The Group Numbers chosen, 800–805, were an arbitrary choice by the author. ***Please note that the user takes full responsibility in editing this file.***

800!N-(CB)(DCO)!-62.50!*!*!-71.98!63.94!*!-77.76!55.31!106.90!!
801!N-(C)(DCO)!-75.07!*!*!-42.12!55.74!112.91!-72.74!45.99!51.97!!
802!N-(CD)(DCO)!-40.32!*!*!*!*!*!*!*!!
805!CO-(N)(O)!-125.22!*!*!-159.57!*!*!-176.70!88.56!*!!