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The thermochemistry of TNAZ (1,3,3-trinitroazetidine) and related species: models for calculating heats of formation

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Abstract

The heats of formation of TNAZ(1,3,3-trinitroazetidine) and related compounds have been calculated with the B3LYP/6-31G(d,p) model to give a mean absolute deviation of 3.1 kcal/mol for 18 singlet species and 5.1 kcal/mol for 12 free radical intermediates. A minimal seven-parameter atom/group additivity scheme was developed that reduces these errors to 1.1 and 1.3 kcal/mol, respectively. Based on these calculations a set of structural enthalpy increments was compiled that allows the precise estimation of heats of formation of highly nitrated species from simpler ones via isodesmic reactions that are independent of atom/group additivity parameters. In a parallel analysis, an augmented Benson group-additivity scheme was developed that allows facile estimation of the heats of formation of the several nitroazetidines as well as related radical species with a precision that is comparable to that obtained via quantum mechanical calculations. In the final section measured activation energies for the initial fragmentation steps, for eight species, are compared with the computed enthalpies for dissociation. The computed lowest energy structures for eleven species are summarized in an appendix. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Heats of formation; TNAZ(1,3,3-trinitroazetidine); Benson group-additivity scheme

1. Introduction

TNAZ(1,3,3-trinitroazetidine) is a “new generation” explosive [1]. The primary focus of our program has been a detailed investigation of the gas phase pyrolysis of TNAZ. As our studies progressed [2], it became evident that unraveling that complex decomposition mechanism would be facilitated by the availability of comparable kinetic data for simpler model compounds. In particular, we were challenged to develop a rational, internally consistent set of thermochemical and kinetic parameters for nitroalkanes that

are structurally related to TNAZ, based on a theoretical model that could be used both to predict the energies of the species involved in the decompositions and to offer insights into the structural basis for those energies. This report consists of four related sections: (A) Density functional theory (DFT) calculations at the B3LYP/6-31G(d,p) level provide estimates of the enthalpies of formation of the parent species and of the first generation of free radicals. The derived $\Delta H_{\text{dis}}^\circ$ are essential guidelines for interpreting the measured E_a s. As a bonus, the calculations provided estimates of the molecular frequencies and therefore ideal gas entropies. Brief comments on the lowest energy structures are appended. (B) An analysis of the structural dependence of the calculated enthalpies for a variety of isodesmic reactions provides a structural ansatz for

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the energies. The derived parameters allow remarkably precise estimates of enthalpies of highly nitrated species from the energies of simpler reference compounds. (C) The Benson group additivity parameters were augmented to yield a simple model for estimating heats of formation of various nitroazetidines. Excellent agreement was found between the experimentally based Benson group additivity scheme and the DFT calculations. A modified Benson scheme for radicals yielded excellent estimates of enthalpies of formation of the radical species. (D) A summary of recently measured kinetic parameters is presented for eight species that incorporate N–NO₂ units and five that contain C–NO₂ groups. From the temperature dependent rates of loss of the parent species, expressed as unimolecular rate constants, activation energies were derived and these are compared with the calculated enthalpies for dissociation.

2. Computational model

The BAC-MP4 model developed by Melius [3] is remarkable for its use of a relatively small basis set, combined with bond additivity corrections, to permit rapid calculations of ΔH_f° with a precision approaching accuracies provided by the far more resource demanding G2 method of Pople [4]. The essence of the BAC-MP4 method is to determine the lowest energy geometry of a molecule at the 6-31G(d) level, compute the single point MP4/6-31G(d) energy, and finally add a series of bond length dependent energy corrections; where appropriate, spin related corrections are also added. Because of the limited capability of MP4 to capture the full correlation energy, the added corrections are necessarily huge (52 kcal/mol in the case of nitromethane).

In spite of the general success of BAC-MP4, the MP4 portion was deemed too resource demanding for the larger molecules in the present study. We turned to the hybrid DFT method B3LYP/6-31G(d,p) (as implemented in the GAUSSIAN 98 suite of programs [5]), which captures more of the correlation energy than does MP4 and scales relatively gradually with molecular size. Politizer [6,7] employed the density functional generalized gradient approximation

CGA/DZVPP model, using the program deMon, to calculate the energies of several nitroazetidines. The 6-31G(d,p) basis set is approximately equivalent to DZVPP; the more recently developed hybrid B3LYP functional should be superior to CGA.

Each structure was optimized at that level; in all cases the optimized structures showed only positive frequencies. The zero point energies and enthalpic thermal corrections to 298.15 K were calculated at the same level; the frequencies are unscaled. The calculated ionization enthalpies (298.15 K) of H¹, C³, N⁴, O³ were (in au): –0.498856, –37.843920, –54.582129 and –75.058263, respectively. The corresponding standard atomization enthalpies were (in kcal/mol): 52.10, 171.29, 112.98 and 59.56. Comments on interesting structural features are assembled in Appendix A.

As with the MP4 model, additive empirical atomic/group corrections were included. However, since the B3LYP/6-31G(d,p) energies were close to the experimental values there was no need for the corrections to include bond distance dependencies. The additive empirical corrections were evaluated by a least squares minimization of the maximum deviation of the calculated heats of formation from the available experimental values using the add-in Solver procedure in the Excel spreadsheet program.

The species studied included various compounds related to TNAZ in their ground states as well as radicals generated by removal of a group or a hydrogen atom. In addition, a number of simpler molecules were calculated to provide calibration points for the evaluation of the additive parameters. In total 24 ground state and 20 radical species were considered. The results are assembled in Tables 1 and 2.

3. Calculated and corrected ground state enthalpies of closed shell species

The first 18 entries in column four of Table 1 are the calculated reference enthalpies of formation (at 298 K) selected to establish the atomic/group additivity corrections. These enthalpies were evaluated using zero point thermal energies (unscaled frequencies) combined with the corresponding enthalpies for the atoms H, C, N and O. The experimental

Table 1

Calculated B3LYP/6-31G(d,p) ground-state energies with and without empirical corrections (298.15 K)

Compound	E_c^a	E_0^a	Calculated ^b ΔH_f°	Corrected ^c ΔH_f°	Experimental	S^0 (eu)
Methane	−40.52401	−40.47899	−21.66	−18.08	−17.78	47.2
Ethane	−79.83874	−79.76381	−25.06	−20.37	−20.03	54.4
Propane	−119.15537	−119.05165	−30.09	−24.27	−25.02	64.2
Cyclobutane	−157.22445	−157.11339	4.26	8.77	6.79	65.7
Ammonia	−56.55777	−56.52332	−9.11	−8.74	−10.98	46.0
Methylamine	−95.86369	−95.79946	−7.12	−5.62	−5.50	57.3
Dimethyl amine	−135.17402	−135.08138	−8.47	−5.85	−4.45	64.7
Ethyl amine	−135.18407	−135.09109	−14.57	−11.95	−11.33	64.8
Nitromethane	−245.01337	−244.96341	−18.73	−18.44	−17.76	70.3
Dinitromethane	−449.48992	−449.43689	−8.60	−11.59	−14.08	85.1
Nitroethane	−284.33496	−284.25620	−26.86	−25.44	−24.45	75.2
1-Nitropropane	−323.65123	−323.54395	−32.21	−29.66	−29.59	77.1
2-Nitropropane	−323.65545	−323.54838	−34.45	−31.91	−33.22	81.6
2,2-Dinitropropane	−528.14079	−528.03176	−30.38	−31.12	−28.84 ^d	93.3
Nitrobenzene	−436.75852	−436.65509	17.07	13.22	16.13	81.8
Nitroamine	−261.03782	−260.99834	−0.71	2.33	1.60 ^e	64.1
N-nitrodimethyl-amine	−339.66462	−339.56920	−7.18	−1.88	1.15	80.3
Azetidine	−173.24916	−173.14923	22.06	23.37	23.47	65.1
N-Nitroazetidine	−377.74459	−377.64176	20.31	24.29		78.8
3-Nitroazetidine	−377.74626	−377.64346	19.34	17.36		81.0
1,3-Dinitroazetidine	−582.23538	−582.13014	21.35	22.06		94.3
3,3-Dinitroazetidine	−582.22977	−582.12503	24.71	19.46		95.5
1,3,3-Trinitroazetidine	−786.71363	−786.60666	29.88	27.30		108.2
		MAD	3.08	1.11		
		Rms	2.67	1.31		
		Max dev	6.03	2.91		

^a Hartrees.^b In kcal/mol.^c With additive atomic/group energy corrections (see text).^d Estimated from the enthalpy of formation of the liquid, combined with the heat of vaporization of 1,1-dinitropropane.^e G2 calculation (see text).

gas phase enthalpies in column five were taken from the Pedley et al. collection [8], unless otherwise noted in the footnotes to Table 1. Two compounds with questionable experimental heats of formation are dinitromethane and 2,2-dinitropropane. Based on (still incomplete) higher-level G3MP2B3 calculations we suspect that the experimental heat of formation of dinitromethane is too negative by 4 kcal/mol and that of 2,2-dinitropropane is too positive by 4 kcal/mol. Even if these drastic changes were incorporated into the present analysis, none of the qualitative conclusion would change. The experimental ΔH_f° of nitroamine, NH_2NO_2 , was assigned the value calculated using the high accuracy G2 method of Pople et al. [4]. The G2 model, applied to the standard G2 set of 125 energies, for a wide variety of

species, has an average absolute deviation from experiment of 1.21 kcal/mol, and is as reliable as several of the experimental values used in the present study.

The minimized root mean square deviation of ΔH_f° for these 18 molecules using the B3LYP/6-31G(d,p) model is 2.7 kcal/mol and the MAD (mean absolute deviation) is 3.1 kcal/mol. These magnitudes are in line with the rms and MAD values for similar computational models based on much larger and broader reference sets. Thus it appears that the procedure used here is reasonably accurate and that the 18 selected compounds are essentially unbiased.

Although the B3LYP/6-31G(d,p) model gave good results, it was of interest to determine if these could be improved by inclusion of empirical additive

Table 2

Calculated B3LYP/6-31G(d,p) radical ground-state energies with and without empirical corrections (298.15 K)

Radical	E_e^a	E_0^a	Calculated ^b ΔH_f°	Corrected ^c ΔH_f°	Experimental	S^0 (eu)
Hydrogen	−0.50027	−0.50027	52.10	52.10	52.10	27.4
Nitro	205.07221	205.06338	5.65	7.91	7.91	57.4
Methyl	39.84288	39.81312	31.78	35.75	36.31	50.2
Ethyl	79.16521	79.10576	23.62	28.71	28.40	61.1
1-Propyl	118.48114	118.39256	19.27	25.48	23.90	70.0
2-Propyl	118.48822	118.39997	14.68	20.90	22.0	70.1
Cyclobutyl	156.55558	156.46013	49.99	54.89	51.14	69.8
Amino	55.87898	55.86002	42.56	47.21	45.5	46.5
Methylamino	95.19808	95.14919	36.42	42.19	43.17 ^d	58.5
Dimethylamino	134.51747	134.44025	29.56	36.47	38.70 ^d	69.3
Nitromethyl	244.34232	244.30712	28.50	29.18	30.40 ^d	67.1
Phenyl	231.56922	231.48173	81.36	81.18	81.00	70.2
2-Nitro-2-propyl	323.00270	322.91060	0.98	3.9	2	81.7
Azetidin- <i>N</i> -yl	172.59341	172.50838	59.75	65.34		67.4
Azetidin-3-yl	172.57755	172.49298	69.52	71.21		67.4
3-Nitroazetidin- <i>N</i> -yl	377.09075	377.00272	56.92	59.23		83.3
3-Nitroazetidin-3-yl	377.08658	376.99842	59.72	58.13		82.7
<i>N</i> -Nitroazetidin-3-yl	377.07120	376.98353	68.90	73.27		80.3
3,3-Dinitroazetidin- <i>N</i> -yl	581.57206	581.48229	63.55	62.57		98.0
3-Nitro- <i>N</i> -Nitroazetidin-3-yl	581.57105	581.48037	64.64	65.74		95.8
Excluding H and NO ₂						
MAD			5.06	1.32		
Rms			2.65	1.68		
Max.Dev.			9.14	3.21		
				N = 8		

^a Hartrees.^b In kcal/mol.^c With additive atomic/group energy corrections (see text).^d G2 calculation (see text).

atomic/group corrections. The formulation tested was

$$\begin{aligned} \Delta H_f^\circ(\text{corrected}) = & \Delta H_f^\circ(\text{calculated}) + n_H P(H) \\ & + n_C P(C) + n_N P(N) + n_{C-N} P(C-NO_2) \\ & + n_{N-N} P(N-NO_2) \end{aligned} \quad (1)$$

where n_H is the number of H atoms in the molecule and $P(H)$ is the corresponding empirical constant, etc. The n_{C-N} term is the number of groups attached to carbon and n_{N-N} is the number of nitro groups attached to nitrogen. With these definitions there is no need, for the set of molecules studied, to employ a correction term for oxygen. The minimized MAD values (in kcal/mol) found for these parameters are the five entries in the left column of Table 3. Inclusion of these empirical corrections produces a dramatic

reduction in the MAD (1.1 kcal/mol) and rms (1.3 kcal/mol) values, with a maximum deviation of 2.9 kcal/mol (dinitromethane). This precision is comparable to what would be expected from the more sophisticated and computationally expensive G2 model of Pople et al. [4] It is important to recognize that while this exceptional fit is due in part to

Table 3

Empirical parameters to correct the calculated B3LYP/6 31G(d,p) energies

Parameter	Value (kcal/mol)	Parameter	Value (kcal/mol)
$P(H)$	1.222	$P(H\text{-rad})$	0.000
$P(C)$	−1.318	$P(NO_2\text{-rad})$	2.260
$P(N)$	−3.229	$P(C\text{-rad})$	1.615
$P(C-NO_2)$	−2.058	$P(N\text{-rad})$	5.507
$P(N-NO_2)$	3.900		

corrections of known model deficiencies, such as anharmonicity in the ZPEs, thermal corrections, as well as residual electron correlation, it also depends on the small number of molecules in the set. Extrapolations should not be undertaken without additional calibration. Small variations in the experimental data or inclusion of new compounds could produce large (compensating) changes in the individual parameters.

Five nitroazetidines are included in Table 1. Their enthalpies of formation are listed in column four and the empirically corrected ΔH_f° s are reported in column 5. One striking difference between the corrected and uncorrected values is the isomeric pair 1,3-dinitroazetidine and 3,3-dinitroazetidine. The 1,3-isomer is predicted to be more stable by direct calculation, but the reverse appears after inclusion of the empirical corrections. Unfortunately, there are no experimental data to distinguish between these contradictory results. For TNAZ the empirical correction suggests a more stable species by about 2.6 kcal/mol. Politzer [6,7] reported a calculated value of 30.7 kcal/mol, which compares well with our value of 29.9 kcal/mol.

4. Calculated and corrected ground state enthalpies of radical species

The first 11 entries in column four of Table 2 are the computed reference enthalpies of formation (at 298 K) of radicals needed to generate additional additivity parameters for radical centers. These enthalpies were evaluated using zero point and thermal energies based on unscaled frequencies, combined with the corresponding enthalpies for the atoms H, C, N and O. With the exceptions noted below the experimental gas phase enthalpies in column six were taken from the NIST data bank [9]. For the cyclobutyl radical we used the Benson value [10], and the “experimental” heats of formation of methylamino, dimethylamino, nitromethyl were assigned the values derived by the Pople G2 method.

Extension of the empirical model to the radical species required four additional parameters. The parameters $P(\text{H-rad})$ and $P(\text{NO}_2\text{-rad})$ are used to make the $\Delta H_f^\circ(\text{H}\cdot)$ and $\Delta H_f^\circ(\text{NO}_2\cdot)$ equal to the experimental

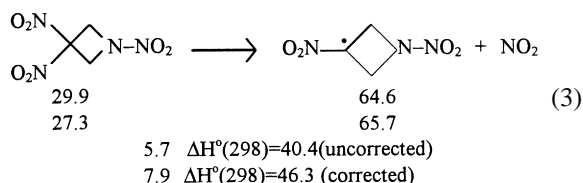
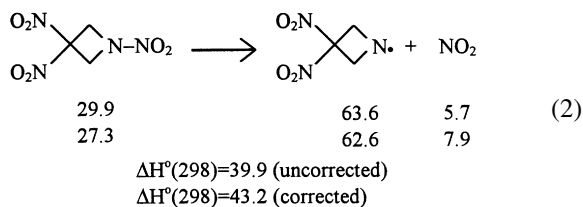
values. The parameters $P(\text{C-rad})$ and $P(\text{N-rad})$ are used for the other radical species (in a least squares sense) to obtain agreement with the experimental data. The first two entries in Table 2 determine $P(\text{H-rad})$ and $P(\text{NO}_2\text{-rad})$; these are 0.00 and 2.26, respectively. The values for $P(\text{C-rad})$ and $P(\text{N-rad})$ were derived by a least squares fit of the residuals (through phenyl) from corrected ΔH_f° s using the atomic parameters determined in the preceding section. $P(\text{C-rad}) = 0.808$ kcal/mol and $P(\text{N-rad}) = 6.248$ kcal/mol (Table 3). The rms value for the seven alkyl and amino radicals, without any empirical correction, is 2.7 kcal/mol, whereas the MAD is 5.1 kcal/mol. The fact that the MAD is so much larger than the rms implies a systematic error in the calculation. After inclusion of the empirical parameters the MAD was reduced to 1.3 kcal/mol and the rms to 1.7 kcal/mol.

The ΔH_f° s of the seven azetidine radicals are reported in column four of Table 2, and the corresponding empirically corrected ΔH_f° s are listed in column five. The large magnitude of $P(\text{N-rad})$ relative to $P(\text{C-rad})$ has the consequence of narrowing or inverting the energy gap between the nitrogen centered radicals and the carbon centered radicals. For example, the 2.6 kcal/mol gap between the 3-nitroazetidin-*N*-yl and *N*-nitroazetidin-3-yl radical is reversed when the corrections are applied.

5. Interpretation of the energetic consequences of several structural features

In formulating a pyrolysis mechanism for TNAZ the first step is still undetermined: does *N*-nitro cleavage dominate over *C*-nitro cleavage or do they dissociate at comparable rates? (The latter assumption was made in the initially proposed mechanism [2].) From the calculated energies of the ground state of TNAZ and of the radical species listed in Tables 1 and 2 it appears that the uncorrected magnitudes of the two $\Delta H_{\text{diss}}^\circ$ are closely balanced (39.3 vs. 40.4 kcal/mol, column four); with the corrections these increase slightly to 43.2 (for 3,3) vs. 46.3 (for 3,*N*) kcal/mol. According to the latter the enthalpy increment for *N*-nitro cleavage is 3.2 kcal/mol lower than for *C*-nitro.

Diagrammatically



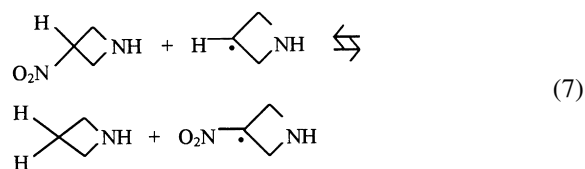
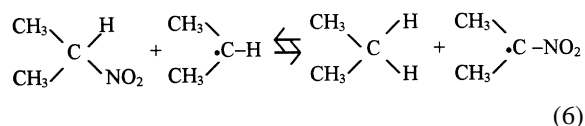
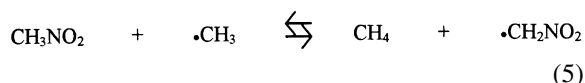
From the values listed in Tables 1 and 2, the average enthalpy increment for dissociation of *N*-nitroazetidine, nitroamine, and *N*-nitrodiethylamine is 45.5 ± 2.3 kcal/mol. When the empirical corrections are included (column five) this increases to 49.3 ± 2.3 kcal/mol. Similarly, the average enthalpy for *C*-nitro dissociation of nitromethane, nitroethane, 1-nitropropane, 2-nitropropane and 3-nitroazetidine is 56 ± 0.6 kcal/mol, which increases to 61.9 ± 0.6 kcal/mol upon inclusion of the empirical parameters. Thus it appears that *N*-nitro dissociation requires significantly lower excitation than does *C*-nitro dissociation (10.5 kcal/mol, both with and without corrections). Clearly the derived small difference in dissociation enthalpies for TNAZ is due to structural features other than the inherent *C*-nitro and *N*-nitro bond energies [11]. These are uncovered in the following model. Suppose

$$\begin{aligned}
 \Delta H(\text{calc}) &= \Delta H(\text{bond energies}) \\
 &+ \Delta H(\text{structural increments})
 \end{aligned} \quad (4)$$

where the structural increments are composed of three components: (1) a term for the stabilization of a carbon radical center by an attached group, $h(\text{C}-\text{NO}_2)$; (2) a term for the repulsive interaction of geminal groups, $h(\text{gem-dinitro})$; and (3) a repulsive interaction for a pair of groups on opposite sides of the azetidine ring where the included angle between the axes of the *C*-*N* bonds is θ , $h(1,3-\theta)$.

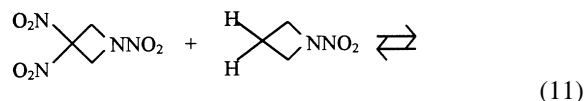
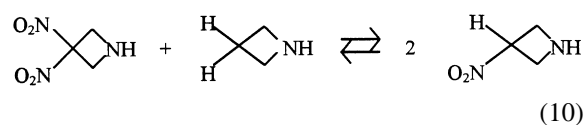
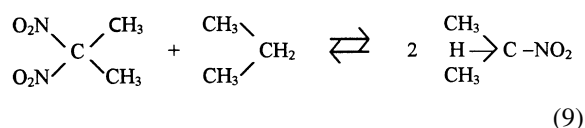
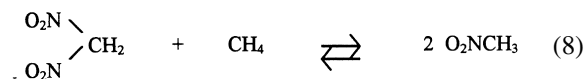
The following three isodesmic exchange reactions provide a value for $h(\text{C}-\text{NO}_2)$. Note that because these are isodesmic conversions the energies are inde-

pendent of the empirical correction parameters as they are defined.



An average stabilization energy derived from Tables 1 and 2 is $h(\text{C}-\text{NO}_2) = -7.5 \pm 1.2$ kcal/mol.

The geminal dinitro (gem-dinitro) interaction contribution can be evaluated in a similar fashion from the following four isodesmic exchange reactions.



The average gem-dinitro interaction energy, $h(\text{gem-dinitro}) = +7.8 \pm 0.5$ kcal/mol. We postulate that the 1,3-dipolar interaction energy has a point dipole form

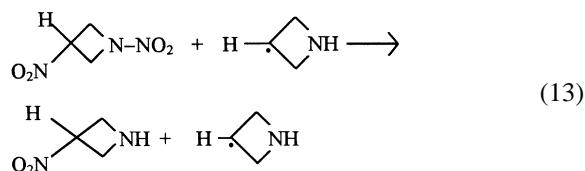
$$h(1,3-\theta) = J^* \cos(\theta) \quad (12)$$

where θ is the angle between the point dipoles

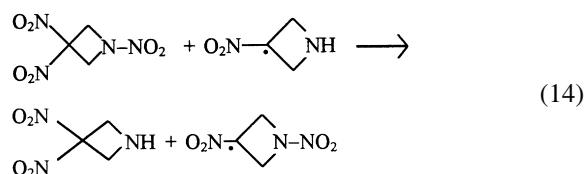
centered at the *N*-nitro and the *C*-nitro groups, and *J* is a scaling constant, which subsumes distributed dipole and effective dielectric constant contributions. Thus, in 3,*N*-dinitroazetidine θ was taken to be 120° , whereas for the radical 3, *N*-dinitroazetidin-3-yl $\theta = 180^\circ$.



In order to estimate the magnitude of *J*, consider the following hypothetical isodesmic exchange.



In this reaction all of the other parametric correction terms and structural features cancel except for $h(1,3 - \theta)$. From the values listed in Tables 1 and 2, the derived 1,3 dipolar interaction energy is 2.63 kcal/mol. Thus the value of $J = 5.26$ kcal/mol. To test this evaluation for the 1,3 dipolar interaction consider the exchange:



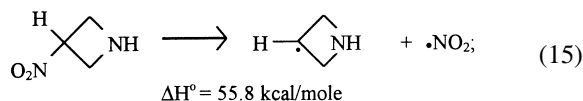
In TNAZ there are two 1,3-dinitro dipolar interactions (total magnitude $2(-5.26) \cos(120) = +5.26$ kcal/mol), whereas in the dinitro radical on the right the dipolar interaction is $\{1(-5.26) \cos(180) = +5.26\}$. Thus for this hypothetical reaction the calculated ΔH° should be close to zero. Indeed, from the magnitudes listed in Tables 1 and 2, $\Delta H^\circ = -0.3$ kcal/mol.

In summary three structural terms contribute to the enthalpy:

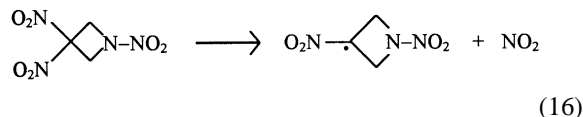
$$\begin{aligned} h(\text{C}-\text{NO}_2) &= -7.5 \pm 1.2 \text{ kcal/mol;} \\ h(\text{gem-dinitro}) &= +7.8 \pm 0.6 \text{ kcal/mol;} \\ \text{and} \\ h(1,3 - \theta) &= -5.3 \text{ kcal/mol.} \end{aligned}$$

Application of the three interaction energy terms

provides a rationale for the near equality of the two NO_2 dissociation steps of TNAZ. Start with the “reference” reaction:



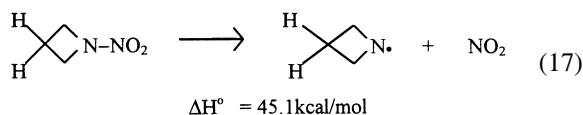
and derive from it the energy for the *C*-nitro dissociation of TNAZ.



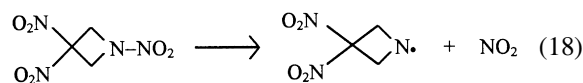
The non-canceling energy terms that enter are (kcal/mol):

	Uncorrected	Corrected
Reference energy	55.8	61.8
<i>C</i> -nitro stabilization	−7.5	−7.5
Gem-dinitro effect	−7.8	−7.8
1,3 Dipole interaction	0.0	0.0
Predicted energy of <i>C</i> – NO_2 dissociation	40.5	46.5
Direct calculation	40.4	46.4

In a similar manner, for the *N*-nitro dissociation use the reference reaction



Then, for the *N*-nitro dissociation of TNAZ



the non canceling energy terms are (kcal/mol):

	Uncorrected	Corrected
Reference energy	45.1	49.0
$2 \times 1,3$ Dipole interaction	−5.3	−5.3
Predicted energy of <i>N</i> – NO_2 dissociation	39.8	43.7
Direct calculation	39.3	43.2

Table 4

Benson-derived heats of formation and corrected DFT values for ground state species

Compound	Benson-derived estimate (kcal/mol)	Corrected DFT estimate (kcal/mol)	Difference (kcal/mol)
Azetidine	23.47	23.37	0.10
<i>N</i> -Nitroazetidine	27.32	24.29	−3.03
3-Nitroazetidine	15.60	17.36	1.76
1,3-Dinitroazetidine	22.10	22.06	0.04
3,3-Dinitroazetidine	19.96	19.46	−0.50
1,3,3-Trinitroazetidine	29.11	27.30	−1.81
		Mean	−0.57
		MAD	1.21

This striking agreement is not the result of a circular argument. A value for TNAZ entered only as one of four examples used to evaluate the gem-dinitro effect. Had TNAZ been omitted, that parameter would have changed by only 0.1 kcal/mol (to 7.9 kcal/mol, which would have improved the agreement). We conclude that in general *N*-NO₂ cleavage does require a lower dissociation energy than C–NO₂ by about 10 kcal/mol. However, the three structural features: *C*-nitro stabilization, gem-dinitro effect and 1,3-dipole interaction terms combine to nearly equalize the two in TNAZ.

When the six atomic/group parameters, *P*(H) etc, are included (values in column five), the corrected NO₂ dissociation energies of TNAZ are virtually unchanged with the *N*-nitro dissociation favored by about 1.3 kcal/mol. Since the three structural energy terms are independent of the empirical parameters this near equality is not affected.

6. Extension of Benson additivity scheme

In Section 4 the heats of formation were calculated using the B3LYP/6-31G(d,p) DFT model that were in good agreement with the available experimental data (MAD 3.1 kcal/mol). These values were then augmented with relatively small additive empirical corrections to give significantly improved heats of formation (MAD 1.1 kcal/mol). In Section 5 it was demonstrated that the calculated heats of formation of highly nitrated azetidines could be reproduced closely from the DFT results for small systems when combined with empirical additive contributions. The question explored in this section is whether the

heats of formation could be adequately reproduced solely by an additive bond energy scheme. We started with the 1976 Benson group/additivity scheme [10] and supplemented it with values for

$$\text{C}-(\text{NO}_2)(\text{C})_2(\text{H}) = -12.80;$$

$$\text{C}-(\text{NO}_2)_2(\text{C})_2 = -8.44; \text{N}-(\text{NO}_2)(\text{C})_2 = 19.25,$$

which were determined by fitting the experimental heats of formation of 2-nitropropane, 2,2-dinitropropane, and *N*-nitrodimethylamine (Table 1). Using this set, the ring strain correction azetidine (1976) = 26.2 kcal/mol and the presently derived 1,3-dipole interaction term $[(-5.3 \cos(\text{included angle}))]$, the values in Table 4 for azetidine and its nitro derivatives were obtained. These Benson derived enthalpies are based entirely on experimental data (except for the

Table 5

Benson parameters for estimating heats of formation of radical intermediates

Parameter	Value (kcal/mol) ^a	Origin ^b
C–(C [*])(H) ₃	−10.08	Retained (1976)
C–(C [*])(C)(H) ₂	−4.95	Retained (1976)
C–(C [*])(C) ₂ (H)	−1.90	Retained (1976)
C [*] –(C)(H) ₂	38.94	Revised
C [*] –(C) ₂ (H)	41.70	Revised
C [*] –(C) ₃	41.24	Revised
C [*] –(C) ₂	58.4	Retained (1976)
C–(N [*])(C)(H) ₂	−6.60	Retained (1976)
C–(N)(C [*])(H) ₂	−6.60	Assumed
C [*] –(NO ₂)(C) ₂	27.33	B3LYP fitted

^a To be used with the 1976 Benson parameters.

^b The revised values were derived by fitting new experimental heats of formation.

Table 6

Experimental rate constants for the decomposition of nitro-compounds

Compounds	Method	Conditions	log A	E_a (kcal/mol)	Mechanism	Reference
CH ₃ NO ₂	Shock tube	900–1500 K	16.25(k_{∞})	58.5(k_{∞})	C–NO ₂ fission	[16]
		5–20 atm	17.1(k_0)	42.0(k_0)		
C ₂ H ₅ NO ₂	IRMPD			55.5	C–NO ₂ isomerization	[17]
C ₂ H ₅ NO ₂	Shock-tube	900–1350 K	15.9	57.0(k_{∞})	C–NO ₂ fission	[18]
		Static	11.53	41.5	HONO elimination	
2-C ₃ H ₇ NO ₂	Shock-tube	900–1150 K	14.6	54.2	C–NO ₂ fission	[20]
		Static	11.3	40.5	HONO elimination	
1-C ₃ H ₇ NO ₂	IRMPD			45	HONO elimination	[17]
1-C ₃ H ₇ NO ₂	Static	483–713 K	11.73	41.5	HONO elimination	[23]
		Shock-tube	915–1200 K	15.4	C–NO ₂ fission	
(CH ₃) ₂ C(NO ₂) ₂	Shock-tube	950–1150 K	13.1	45.7	C–NO ₂ fission	[20]
(CH ₃) ₂ NNO ₂	Static & shock tube	460–960 K	15.9	43.7	N–NO ₂ fission	[24]
		Pulsed laser	800–900 K	13.5	N–NO ₂ fission	
(C ₂ H ₅) ₂ NNO ₂	IRMPD				N–NO ₂ fission	[26]
(C ₂ H ₅) ₂ NNO ₂	Static	180–240°C	15.1	41.6	N–NO ₂ fission	[28]
		70–350 torr				
CH ₃ NHNO ₂	Static	493–553 K	13.65	41.0	N–NO ₂ fission	[29]
		97–192 torr				
C ₂ H ₅ NHNO ₂	Static	493–553 K	13.69	41.8	N–NO ₂ fission	[29]
		97–192 torr				
C ₃ H ₇ NHNO ₂	Static	493–553 K	14.89	45.2	N–NO ₂ fission	[29]
		97–192 torr				
<i>i</i> -C ₃ H ₇ NHNO ₂	Static	493–553 K	13.55	41.3	N–NO ₂ fission	[29]
		97–192 torr				
<i>n</i> -C ₄ H ₉ NHNO ₂	Static	493–553 K	15.34	45.8	N–NO ₂ fission	[29]
		97–192 torr				
<i>i</i> -C ₄ H ₉ NHNO ₂	Static	493–553 K	14.61	43.7	N–NO ₂ fission	[29]
		97–192 torr				
Azetidine	Shock tube	855–1100 K	14.98	54.8	C–N fission	[30]
TNAZ	Shock-tube	750–1100 K	14.0	39.54	N–NO ₂ or C–NO ₂ fission	[31]
C ₆ H ₅ NO ₂	Shock-tube	1070–1180 K	15.3	68.2	C–NO ₂ fission	[32]

minor 1,3-dipole correction). The mean value of the difference between Benson derived energies and the corrected DFT energies is only 1.1 kcal/mol, which demonstrates that there is little difference in bias between the two approaches and probably little bias in either individually. The MAD (1.7 kcal/mol) is also small. Given the established uncertainty in the DFT magnitudes, these evaluations indicate that the Benson scheme is an equally valid way for estimating heats of formation. By adjusting the azetidine ring strain correction, the MAD could be reduced to 1.2 kcal/mol.

Extension of the Benson procedure to the radical species is more complicated because, as Doering [12] has pointed out, the Benson parameters for carbon

radical centers were based on old experimental data that yields heats of formation systematically too low by about 2.5 kcal/mol [12]. We derived revised values using the enthalpies of formation of ethyl, 1-propyl, 2-propyl, 2-methyl-1-propyl, 2-butyl, and 2-methyl-2-propyl radicals given in the NIST standard reference data [9]; these are listed in Table 5. The rms error for the fit is 0.5 kcal/mole, which is as good as the reported experimental uncertainties. The Benson values for nitrogen centers were retained. With these parameters it was found that the Benson-estimated enthalpies of formation of azetidin-*N*-yl, 3-nitroazetidin-*N*-yl and 3,3-dinitroazetidin-*N*-yl radicals, when compared with the corrected B3LYP values, gave a MAD = 2.1 kcal/mol. Since these parameters are

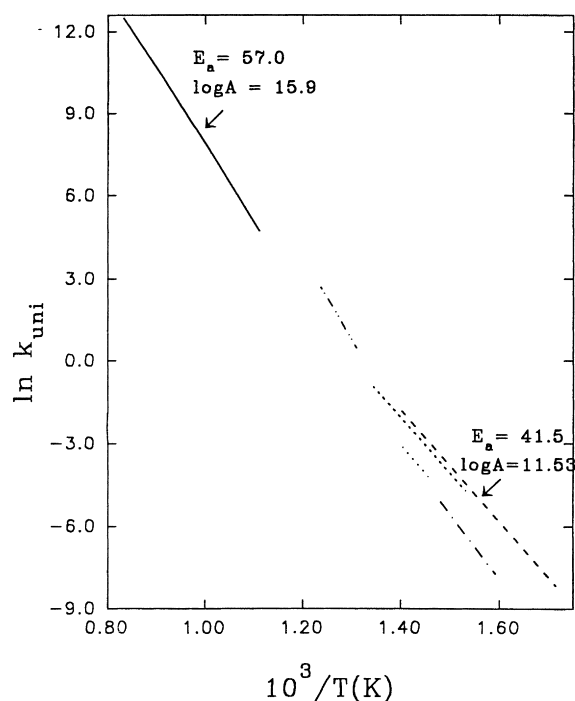


Fig. 1. Unimolecular rate constant for the thermal decomposition of nitroethane. The data are from the following authors: (—) Glanzer and Troe [16]; (---) Frejacques [19]; (- - -) Wilde [33]; (.....) Geiseler et al. [34]; (- · - · -) Cottrell et al. [35]; (- · - · - · -) Wilde [36].

based entirely on experimental data, the internal consistency is satisfying. To calculate the Benson enthalpies of formation of the remaining four azetidinyl radicals, two more parameters are needed. We assumed that $C-(N)(C^*)(H)_2 = C-(N^*)(C)(H)_2 = -6.6$ kcal/mol, and the missing value for $C^*-(NO_2)(C)_2$ was obtained by maximizing the fit of the four Benson values against the four corrected B3LYP values. This gave a MAD = 1.9 kcal/mol, which is satisfactory.

We conclude that a Benson group parameter approach leads to enthalpies of formation that are comparable to those obtained by our DFT calculations.

7. Selected background kinetic data

Temperature dependent pyrolysis rates (in the gaseous state) have been reported for eight species

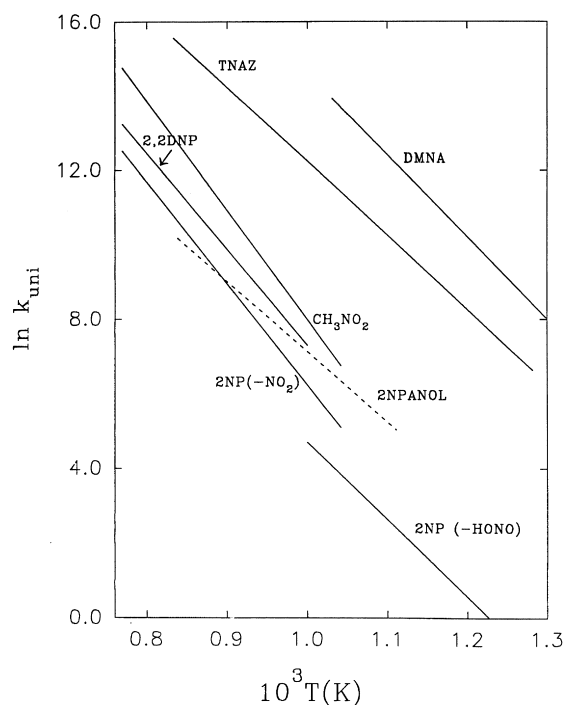


Fig. 2. Unimolecular rate constants for the thermal decomposition of nitro-compounds. The designations in the figure are: DMNA—dimethylnitramine; TNAAZ—1,3,3-trinitroazetidine; 2,2DNP—2,2-dinitropropane; 2NPANOL—2-nitropropanol; 2NP(-NO₂)—2-nitropropane decomposition through N-NO₂ fission; 2NP(-HONO)—2-nitropropane decomposition through HONO elimination.

that incorporate N-NO₂ units and five that contain C-NO₂ groups. These experimental results were expressed as unimolecular dissociation rate constants. Table 6 is a selected compilation of the kinetic parameters, derived from measurements in shock tubes, static reactors or flow tube reactors. Overall there is general agreement but significant differences for several systems remain, particularly between shock tube data and results derived from flow tube or static reactor experiments wherein surface catalyzed processes cannot be completely eliminated. Typical divergencies are illustrated in Fig. 1 for nitroethane. A compilation of temperature dependent rate constants for the initial fragmentation of six nitroalkanes and dimethylnitramine (shock tube pyrolyses) is plotted in Fig. 2. Per Eyring rate theory, $E_a = \Delta H^\ddagger(\text{dis}) + RT\{m\}$, where $T\{m\}$ is a mean temperature for the range

Table 7

Comparison of E_{as} (shock tube data) with $\Delta H_{\text{dis}}^{\circ}$ (298 K) for NO_2 fission

Compound	E_{a} (kcal/mol)	$\Delta H_{\text{dis}}^{\circ}$ (kcal/mol)
$\text{H}_3\text{C}-\text{NO}_2$	58.5 ± 0.3	60.86
$\text{C}_2\text{H}_5-\text{NO}_2$	57	60.81
$2-\text{C}_3\text{H}_7-\text{NO}_2$	54.2 ± 3.8	59.47
$(\text{CH}_3)_2\text{C}(\text{NO}_2)_2$	45.7 ± 1.7	41.73
$\text{C}_6\text{H}_5\text{NO}_2$	65.6	74.63
TNAZ	39.5 ± 2.4	43.2 (39.9) ^a (N– NO_2 cleavage) 46.3 (40.4) ^a (C– NO_2 cleavage)
$(\text{CH}_3)_2\text{NNO}_2$	43.7 ± 0.4	46.77
Azetidine	54.8 ± 4	C–N (ring)

^a Uncorrected values.

covered by the Arrhenius plot. Generally, $\Delta H^{\ddagger}(\text{dis})$ may be identified with $\Delta H^{\circ}(\text{dis})$, unless there is a basis for suspecting the presence of a barrier in the exit channel or that an intramolecular rearrangement occurs prior to fragmentation. Assuming no such complexity, the values derived from Table 6 are compared in Table 7 with the corresponding magnitudes evaluated from columns five of Tables 1 and 2. Except for 2,2-dinitropropane, the computed enthalpies are several kilocalories larger than the reported activation energies. At this stage we have insufficient information about the energies, geometries and vibrational frequencies for the critical transition structures to undertake full RRKM calculations.

Acknowledgements

The authors express our sincere thanks to the ARO for partial support of these studies under grant # DAAH 04-95-1-0130.

Appendix A

In Tables A1 and A2 we listed computed interatomic distances, bond angles, zero-point energies and entropies of eleven related nitramines and nitro-alkanes. These are converged minimum energy structures derived via B3LYP/6-31G(d,p). The molecular frequencies were not scaled. The zpe and entropies (listed in Table A1) follow a rational sequence with increasing NO_2 substitution.

The former reflects contributions from larger numbers of high frequencies associated with increased NO_2 attachments. In contrast, the vibrational components of the entropies reflect significant changes in the number of low frequencies that develop with increased number of roto-vibrators of moieties attached by single bonds, and/or fluxional oscillations of the azetidine rings.

One surprise appeared in Table A1. Note the relatively long C– NO_2 bond length and the short C–C separation in $(\text{H}_3\text{C})_2\text{C}(\text{NO}_2)_2$ compared with the corresponding values for the other ten species. These converged values appeared whether the initial input parameters were as listed or with the magnitudes reversed. In electron diffraction measurements the two distances could not be resolved; only mean values were quoted [13] for $(\text{H}_3\text{C})_2\text{CHNO}_2$ {1.518 \pm 0.015, Å}; for $(\text{H}_3\text{C})_2\text{C}(\text{NO}_2)_2$ {1.517}; for $(\text{H}_3\text{C})_3\text{CNO}_2$ {1.533}. In 2,2 di-nitro propane, the planes of the two nitro groups are tilted at about 118°, with maximum avoidance of the CH_3 hydrogens. Clearly, both steric and dipolar interactions are reflected in these intergroup separations.

Structural parameters for azetidine derived from microwave data [14] and for TNAZ from its crystal structure [15] are designated a and b in Table A2. For all the listed species, the derived bond angles are mutually consistent, within a few degrees. Estimates of the flap angles in the ring (defined as the dihedral angle between the planes CCC and CNC) and the relative orientations of the NO_2 groups were read from plots of structures based on the converged Z matrices. For azetidine spectroscopic data indicate a flap angle of 30°; the graph value is 27.2°. In *N*-nitro azetidine, the angle is 17.7°, while the plane of the NO_2 group is tilted about 40° relative the approximate plane of the ring. In 3-nitro azetidine, the flap angle appears larger (22.2°) and the plane of the NO_2 group is at a 60° tilt from the plane of the ring, but in the 3,3 di-nitro species the flap angle is reduced to 17.9°, while the planes of the two NO_2 groups are approximately normal to each other. The flap angle is further reduced in the 1,3-di-nitro compound. The two-nitro groups are tilted in opposite directions at about 40° with respect to the plane of the ring. Finally, in TNAZ, the computed flap angle is 13.3°, essentially equal to that reported for the crystal [15]. Two NO_2 groups, on opposite sides of the ring, have the same configuration

Table A1

Zero point energies and entropies. Ideal gas, SHO, with unscaled frequencies (298.15 K)

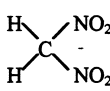
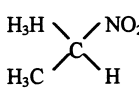
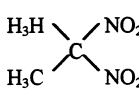


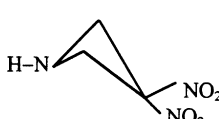
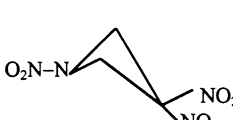
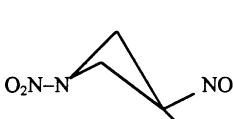
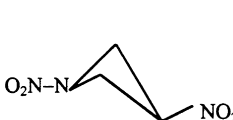
Compound	ZPE (kcal/mol)	S_{total}^0 (eu)	S_{tr}^0	S_{rot}^0	S_{vib}^0
$\text{H}_3\text{C}-\text{NO}_2$	31.35	70.303	38.246	23.576	8.481
	33.28	85.103	39.892	27.196	18.016
	67.19	81.556	39.372	26.504	15.680
	68.42	93.280	40.591	28.567	24.124
	62.71	65.116	38.046	23.441	3.630
	64.51	80.968	39.779	27.097	14.092
	65.74	95.510	40.867	29.142	25.501
	67.12	108.204	41.663	31.032	35.509
	66.06	94.339	40.867	29.549	23.923
	64.53	78.772	39.779	27.044	11.949

Table A1 (continued)

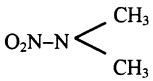
Compound	ZPE (kcal/mol)	S_{total}^0 (eu)	S_{tr}^0	S_{rot}^0	S_{vib}^0
	59.88	80.300	39.406	26.300	14.594

Table A2

Computed intratomic distances (Å) and bond angles (°) [B3LYP/6–31G(d,p)]

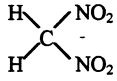
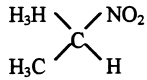
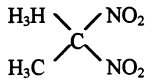
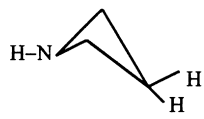
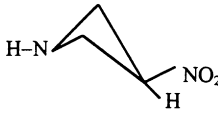
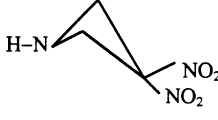


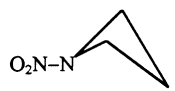
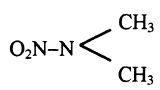
Compound	C–NO ₂	N–O	C–C	(C–N) _{ring}	N–H	N–NO ₂	∠	Ref.
H ₃ C–NO ₂	1.498	1.227					∠ _{ONO} 125.9 ∠ _{CNO} 116.8	
	1.500 1.514	1.224 1.223					∠ _{ONO} 127.4 ∠ _{CNO} 116.7 ∠ _{NCN} 110.3	
	1.525	1.227 1.228	1.527				∠ _{ONO} 125.4 ∠ _{CNO} 117.5 ∠ _{CCC} 113.5	
	1.544	1.224 1.222	1.518				∠ _{ONO} 126.5 ∠ _{CNO} 117.6 ∠ _{NCN} 103.5 ∠ _{CCC} 115.5	
			1.548 1.563	1.484 1.473			∠ _{CCC} ∠ _{CNC} ∠ _{CNC} 91.2	[14]
	1.511	1.227	1.539	1.484	1.015		∠ _{ONO} 125.7 ∠ _{CNO} 117.1 ∠ _{CCC} ∠ _{CNC} 91.3	
	1.516 1.519	1.223	1.539	1.485	1.016		∠ _{ONO} 126.9 ∠ _{CNO} 116.5 ∠ _{NCN} 106.8 ∠ _{CCC} 87.5	
	1.513 1.523 1.497	1.222 1.223	1.542 1.545	1.481 1.485		1.397 1.351	∠ _{ONO} 127.3 ∠ _{CNO} 116.3 ∠ _{NCN} 1073 ∠ _{CCC} 89.2, 90 ∠ _{CNC} 95	[15] [15]

Table A2 (continued)

Compound	C–NO ₂	N–O	C–C	(C–N) _{ring}	N–H	N–NO ₂	∠	Ref.
	1.511	1.225	1.543	1.481		1.387	∠ _{CCC} ∠ _{ONO} 127.6 ∠ _{CNO} 116.8 ∠ _{ONO} 94.0	
		1.230	1.554	1.479		1.381	∠ _{ONO} 127.2 ∠ _{CNC} 93.9 ∠ _{CNN} 120.4 ∠ _{CCC} 88.1	
		1.232		(chain) 1.458		1.385	∠ _{ONO} 125.9 ∠ _{CNC} 120.1 ∠ _{CNN} 115.5	

as in the 1,3 species, while the plane of the third is approximately normal to its gem moiety.

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