



**Property Predictions for Nitrate Salts With  
Nitroxy-Functionalized Cations**

**by Michael J. McQuaid and Gregory W. Drake**

**ARL-TR-5547**

**May 2011**

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Weapons and Materials Research Directorate, ARL**

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14. ABSTRACT To examine a hypothesis that the thermal stability of an organic nitrate salt would correlate with the Gibbs free energy difference [ $\Delta G_r(298)$ ] between it and expected products of the first step of its decomposition, computationally based $\Delta G_r(298)$ estimates were obtained for relevant salts whose responses to thermal loads have been reported. The data acquired generally supports the hypothesis. Considered to be thermally stable if they exhibited <1% mass loss after being held at 75 °C for 24 h or if their decomposition did not onset in a differential scanning calorimetry experiments at a temperature below 150 °C, salts for whom negative $\Delta G_r(298)$ estimates were calculated usually met the criteria while those for whom positive $\Delta G_r(298)$ estimates were calculated usually did not. The results indicate that it is unlikely that nitrate salts having cations with more than two nitroxy groups will be stable for 24 h at 75 °C. Enthalpy of formation and density estimates were also obtained for all salts considered in the study.					
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## 1. Introduction

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With Environment Quality Basic Research (EQBR) and Strategic Environmental Research and Development Program (SERDP) funding, organic salts with nitroxy-functionalized cations were investigated as potential ingredients for solid rocket propellant formulations. (Such cations have chemical structures with the form  $\text{RO}^{\alpha}\text{N}^{\beta}\text{O}_2^{+}$ , where  $\text{O}^{\alpha}\text{N}^{\beta}\text{O}_2$  is the nitroxy group and R is a molecular fragment that is bonded to the nitroxy group's  $\text{O}^{\alpha}$ -atom via an alkyl group C-atom [ $-\text{CH}_n-$ ,  $n = 0, 1, \text{ or } 2$ ]). The motivation and rationale for the effort is provided in more detail elsewhere (McQuaid and Drake, 2010). Briefly, because of the threat ammonium perchlorate poses to human health via its contamination of ground water, the Department of Defense desires alternate oxidizers for high-performance propulsion applications. Organic salts with nitroxy-functionalized cations were identified as a class of compounds with the potential to meet performance requirements while posing less risk to human health and the environment, but candidates from the class that had been synthesized prior to the EQBR effort were too “thermally unstable”<sup>\*</sup> to be employed as rocket propellant ingredients (Dunn, 1952; Naoum and Ulrich, 1929; Medard, 1954; Urbanski, 1965). The EQBR and SERDP efforts were predicated on the thought that the thermal instability of those salts was attributable to them having acidic protons, and that by designing, synthesizing, and characterizing quaternized varieties, viable candidates within the class might be identified.

Results of prior studies conducted under the EQBR program have been reported previously (Drake et al., 2009; McQuaid and Drake, 2010). Figure 1 shows cations of nitrate (anion) salts that were isolated and had various properties characterized (Drake et al., 2009). Of this group, only 2-nitroxy-N, N, N-trimethylethanammonium (**1**) nitrate was found to have thermal stability sufficient for rocket propellant applications. However, having a negative O-atom balance, this salt is a fuel rather than an oxidizer (see section 4).

In a complementary modeling study (McQuaid and Drake, 2010), a hypothesis that the thermal stabilities of salts with nitroxy-functionalized cations might correlate with the length(s) of their  $\text{O}^{\alpha}\text{-N}^{\beta}$  bond(s) was investigated. Predictions for the relative energies and geometries of (equilibrium) conformers of a number of (isolated) neutrals and cations were obtained from a B3LYP/6-31+G(d, p) model, and various correlations between conformer structural characteristics and predictions for conformer energies and  $\text{O}^{\alpha}\text{-N}^{\beta}$  bond lengths were observed. However, a correlation between predicted  $\text{O}^{\alpha}\text{-N}^{\beta}$  bond lengths and thermal stability was not

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<sup>\*</sup>For a candidate to qualify as a propellant ingredient, it must be able to be held (isothermally) at 75 °C for a day and lose <1% of its mass. In this report, that standard is the primary basis for describing a compound as thermally stable or unstable. However, another more commonly reported measure/indication of a candidate's thermal stability is the temperature at which it is observed to decompose in a differential scanning calorimetry (DSC) experiment. Compounds that begin to decompose at temperatures <150 °C in DSC experiments do not typically meet the primary standard. Therefore, such a result is a secondary basis for labeling a compound as thermally unstable. Alternate types of thermal responses, such as the phase changes that compromise ammonium nitrate's usefulness as a rocket propellant ingredient, are not considered here.

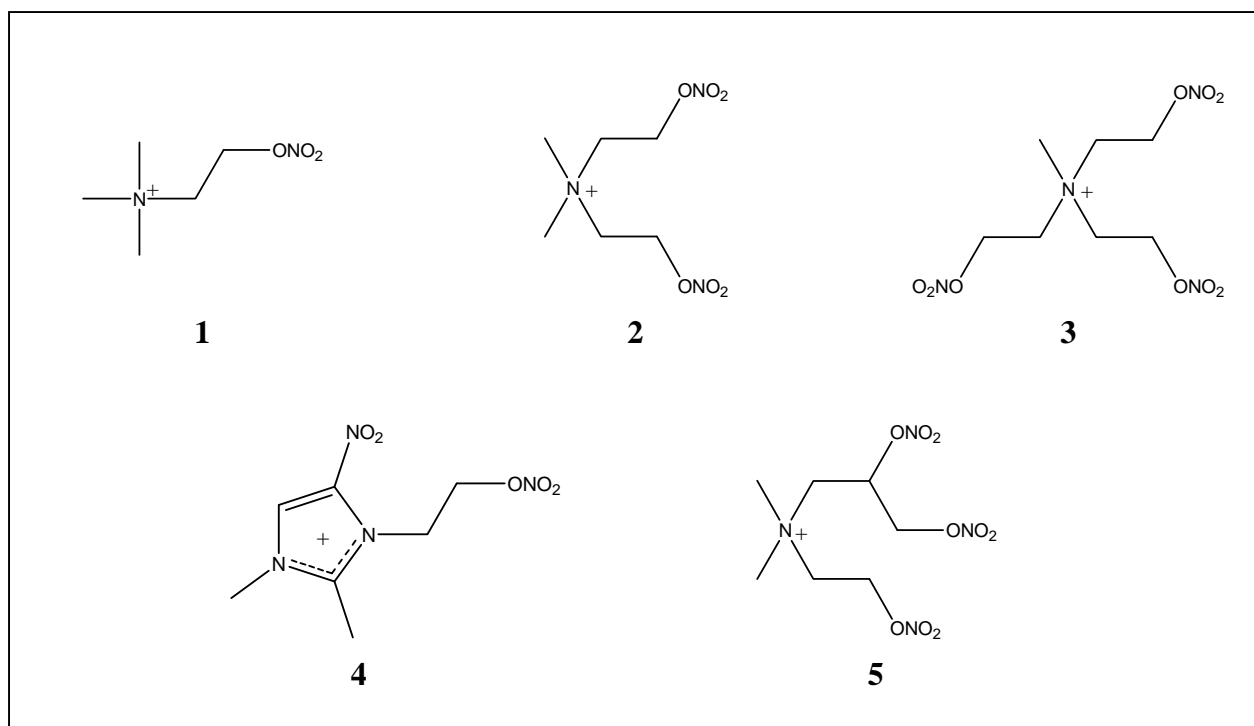
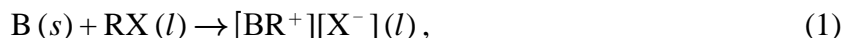


Figure 1. Nitroxy-functionalized cations synthesized by Drake and coworkers.

observed. Molecular structures for notional cations with imidazolium and guanidinium groups were also modeled, but those results (alone) were not considered evidence sufficient to justify an effort to synthesize them.

Following the previous modeling study, an approach for predicting the formation potential of an organic salt from a pair of neutral precursors was identified, and it was thought that it might be applied to obtain predictions for the thermal stabilities of salts of interest. Developed by Gutowski and coworkers (2005, 2007) and validated for ionic liquids with variously functionalized imidazolium cations, the method entails computing the Gibbs free energy change (at 298 K and 1 atm) [ $\Delta G_r(298)$ ] for the (formation) reaction



where B is a proton or methyl cation acceptor (P/MCA) and RX is a proton or methyl cation donor (P/MCD); i.e., R is CH<sub>3</sub> or H. The  $\Delta G_r(298)$  value is obtained by estimating enthalpy and entropy changes [ $\Delta H_i(298)$  and  $\Delta S_i$ , respectively] for steps (*i*) of a Born-Haber (B-H) cycle.

Because the method produces predictions for a system's equilibrium properties, and not its reaction kinetics per se, its results might not be expected to provide reliable predictions for candidate formation potentials or thermal stabilities. However, the rates of decomposition of nitrate salts have been observed to correlate with the dissociation constants [ $K_a(T)$ ] associated with such reactions (Rubtsov et al., 2004), and  $K_a(T)$  and  $\Delta G_r(298)$  are related per

$$K_a(T) = \exp[-\Delta G_r(T)/RT], \quad (2)$$

where  $T$  is the temperature and  $R$  is the universal gas constant. And since Gutkowski et al. (2005) did observe a correlation between formation potentials and  $\Delta G_r(298)$ , an investigation of their method as a means of obtaining predictions for salt thermal stabilities was undertaken.

Figure 2 depicts steps of the B-H cycle Gutowski et al. employed to estimate the total enthalpy change for equation 1–type reactions. These steps include (1) the enthalpies of vaporization ( $\Delta H_v$ ) and/or sublimation ( $\Delta H_s$ ) of the P/MCA and the P/MCD, (2) the proton or methyl cation affinity of  $\text{NO}_3^-$  ( $\Delta H_1$ ), (3) the proton or methyl cation affinity of the P/MCA ( $\Delta H_2$ ), and (4) the lattice enthalpy ( $\Delta H_L$ ) of the salt. (It is assumed throughout this report that all B-H steps occur at 298 K/25 °C and 1 atm.) The figure does not include a step corresponding to the enthalpy change associated with conversion of  $[\text{BR}^+][\text{X}^-] (s)$  to  $[\text{BR}^+][\text{X}^-] (l)$ . All the nitroxy-functionalized ionic compounds that are considered in this study and whose states at 298 K and 1 atm are known are solids. Therefore, that step was not included in the B-H cycles formulated for this study.

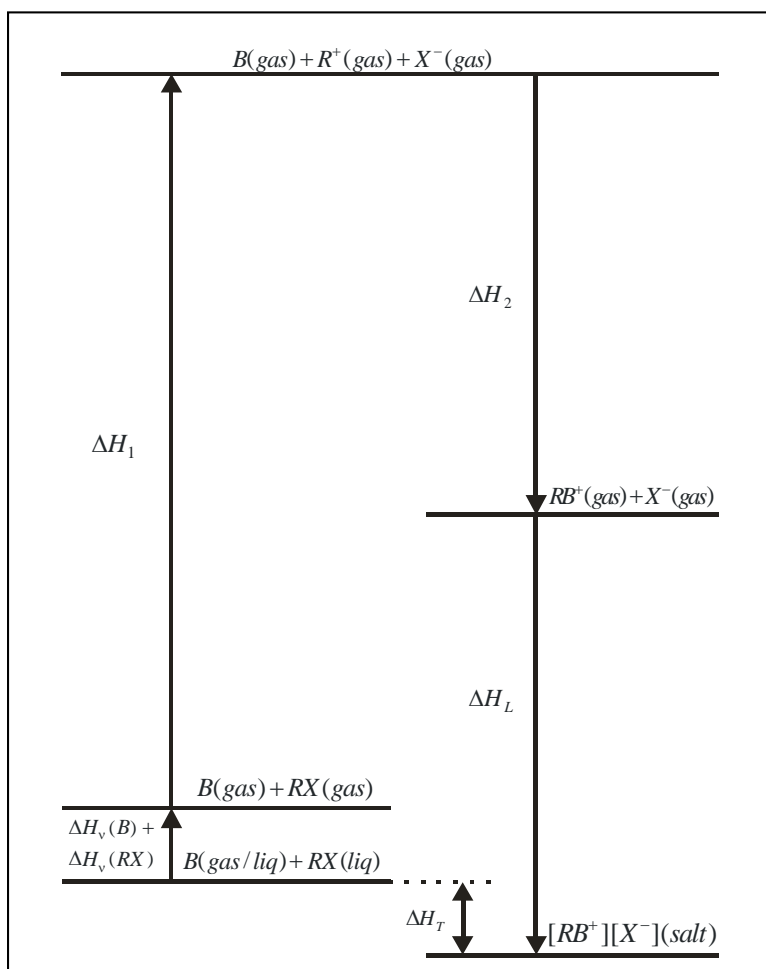
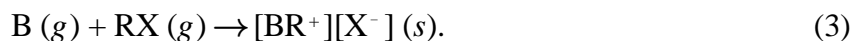


Figure 2. B-H cycle for calculating  $\Delta H_r(298)$  values for equation 1–type reactions.

In developing the method, Gutowski et al. (2005) estimated most of the enthalpy and entropy changes for individual steps via equations that employed input derived from quantum chemistry methods. Using a model developed by Jenkins et al. (1999; 2002) to estimate  $\Delta H_L$ , they found  $\Delta G_r(298)$  (formation) values to be less than +10 kcal/mol for all salts/ILs for whom syntheses had been reported. The discrepancy between the threshold expected based on thermodynamic principles (0 kcal/mol) and the +10 kcal/mol threshold observed was attributed to an uncertainty of  $\pm 10$  kcal/mol in the estimates. Gutowski et al. also observed that salt/IL formation potentials correlated with enthalpies of reaction [ $\Delta H_r(298) = \Delta H_1 + \Delta H_2 + \Delta H_L$ ] calculated for salt production from gas-phase reactants, namely,



Salts/ILs with  $\Delta H_r(298)$  (formation) values  $< -13$  kcal/mol were identified as ones that had been or might be synthesized.

In a subsequent study whose primary focus was the development and validation of a method for estimating the enthalpies of formation [ $\Delta H_f(298)$ ] of azolium salts, Gutowski and coworkers (2007) found that for 1:1 salts with large nonspherical anions, there was significant disagreement between  $\Delta H_L$  values estimated via Jenkins' model and those derived from experimentally measured data. Therefore, they reparameterized the model. Found also by Byrd and Rice (2009) to produce more reliable  $\Delta H_L$  estimates for 1:1 salts with anions of interest, the reparameterized model produces estimates whose magnitudes are 20 to 40 kcal/mol larger than those produced by Jenkins' model. As such, concomitant adjustments to the formation thresholds established in the original study are necessary if the revised model is employed as the basis for estimating  $\Delta H_L$  values.

Because nitroxyalkyl-substituted amines are poor bases, Drake et al. (2009) synthesized their corresponding salts by first quaternizing/methylating their (more basic) hydroxyalkylamine analog, then nitrating the product. As such, equation 1 does not correlate with this two-step process, and the method developed by Gutowski et al. is therefore of limited value with respect to predicting the potential for synthesizing a salt via the two steps. (The method should be capable of predicting the quaternization potential of the hydroxyalkylammonium analogs.) Nevertheless, it was thought that calculated  $\Delta G_r(298)$  values for hypothetical single-step quaternization reactions with methyl nitrate ( $\text{CH}_3\text{ONO}_2$ ) as the MCD might be instructive because they would provide some indication of the potential for the salt (product) to decompose by transferring a methyl cation to the anion. This type of reaction has been indicated as the first step in the thermal decomposition of tetramethylammonium nitrate (Jain et al., 1978).

To determine if  $\Delta G_r(298)$  estimates for equation 1-type reactions would correlate with the aforementioned measures of thermal stability, a slightly modified version of Gutowski et al.'s method was developed and applied to a wide variety of ammonium and azolium nitrate salts whose syntheses have been reported in the open literature. Results for guanidinium and

hydrazinium nitrate were obtained as well. In addition, analogous calculations were performed for notional nitrate salts with other variously functionalized imidazolium, pyrazolium, 1,2,3-triazolium, 1,2,4-triazolium, tetrazolium, and guanidinium cations. Because most of the input needed to estimate the salts'  $\Delta H_f(298)$  values and densities ( $\rho$ ) were generated in the course of producing  $\Delta G_r(298)$  estimates, those parameters were also estimated/predicted. The implications of the results with respect to the prospects for synthesizing salts with nitroxy-functionalized cations that can be utilized for rocket propellant applications are discussed.

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## 2. Computational Methods

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### 2.1 Quantum Chemistry Methods

All the quantum chemistry results that were employed as input for calculating property estimates were obtained from models that combine the B3LYP hybrid functional (Becke, 1993; Lee et al., 1988; Stephens et al., 1994; Vosko et al., 1980) with a 6-31+G(d,p), 6-31G(d,p), or 6-31G(d) basis set (Clark et al., 1983; Petersson et al., 1991; Petersson et al., 1988). The models were implemented via the Gaussian03 suite of quantum chemistry codes (Frisch et al., 2003). B3LYP/6-31+G(d,p) results for cations characterized in the previous EQBR modeling study were reutilized.

For newly considered species, geometry optimizations were performed to predict properties of equilibrium configurations that isolated molecules could acquire. Starting structures for the optimizations were constructed with a graphical user interface-enabled molecular mechanics model (Semichem, Inc., 2008). However, unlike the previous study in which extensive conformer searches were conducted, usually only one conformer of each newly considered molecule was modeled. The decision to perform such limited searches was based on the observation that energy differences between conformers (determined in the previous study) were small in comparison to changes in  $\Delta G_r(298)$  associated with the substitution of a  $-\text{ONO}_2$  or  $-\text{NO}_2$  group for an H-atom. The optimizations' convergence criteria were max. force  $\leq 0.000450$  hartree/bohr, root mean square (RMS) force  $\leq 0.000300$  hartree/bohr, max. displacement  $\leq 0.001800$  bohr, and RMS displacement  $\leq 0.001200$  bohr. For all structures meeting these criteria, normal mode analyses were conducted to establish that they had no imaginary frequencies and thus were indeed equilibrium structures. Subsequently, the zero-point vibrational energies derived from the normal mode analyses were summed with electronic energies and thermal (pressure\*volume) energies to obtain (molar) gas-phase enthalpies at 298 K and 1 atm [ $H_g(298)$ ].

The geometries produced by optimizations performed with the B3LYP/6-31+G(d,p) model were then employed as starting points for optimizations performed with B3LYP/6-31G(d,p) or B3LYP/6-31G(d) models. While little difference between the results from the three models was

expected or observed, optimizations performed with the latter two models were conducted because other models employed to compute various properties were parameterized based on results from them.

## 2.2 Enthalpy of Vaporization and Enthalpy of Sublimation Estimates

In the study reported by Gutowski et al. (2005), it was assumed (for any compound whose physical state at 298 K and 1 atm was not known) that all (neutral imidazole) P/MCAs were solids and that the (neutral) P/MCDs were liquids. With the possibilities of P/MCAs being liquids or of P/MCDs being solids excluded, only  $\Delta H_s$  values for the imidazoles and  $\Delta H_v$  values for P/MCDs were needed as input. To obtain those values, Gutowski et al. derived and employed modeling-based estimates, making no reference to measured values.

In the current study, the only P/MCDs of interest are nitric acid ( $\text{HNO}_3$ ) and methyl nitrate ( $\text{CH}_3\text{NO}_3$ ). Both are liquids at 298 K and 1 atm, and measured  $\Delta H_v$  values have been reported for them (Gray and Pratt, 1957; Wilson and Miles, 1940). (The estimate for  $\text{HNO}_3$  was 3.8 kcal/mol less than the measured value while the estimate for  $\text{CH}_3\text{NO}_3$  was 0.3 kcal/mol less than the measured value.) Seeing no particular reason to use modeling-based estimates for these cases, we employed the measured values.

The situation with the P/MCAs is more complicated. For most of the known salts, the state of the corresponding P/MCA at 298 K and 1 atm is known (with several of them being gases), and for a few of them, measured enthalpies of phase change were identified. Regardless, since the known salts represented validating cases for a method to be employed to predict the thermal stability of notional salts, and the physical state at 298 K of their corresponding bases may also be unknown,  $\Delta H_v$  estimates were obtained and employed for compounds known to be liquids,  $\Delta H_s$  estimates were obtained and employed for compounds known to be solids, and no enthalpy of phase change was included for gasses. For any P/MCA whose state at 298 and 1 atm was unknown, it was assumed it was a solid and a  $\Delta H_s$  estimate was obtained and employed for the calculation of  $\Delta G_f(298)$ . The decision to employ  $\Delta H_s$  for all such cases was based on a lack of confidence in the reliability/accuracy of melting point prediction methods and a desire that any bias that might be introduced from having to choose between  $\Delta H_s$  and  $\Delta H_v$  estimates be consistent for all cases.

The  $\Delta H_v$  and  $\Delta H_s$  estimates were obtained from models developed by Rice et al. (1999). In them,  $\Delta H_v$  and  $\Delta H_s$  are calculated from the area of a molecule's 0.001 electrons/bohr<sup>3</sup> (au) electron isodensity surface (SA) and statistically based measures on that surface of (1) the degree of balance between positive and negative charges ( $\nu$ ) and (2) the variability of the electrostatic potential ( $\sigma^2$ ). Parameterized based on results from a B3LYP/6-31G(d) model, the relationship employed to estimate  $\Delta H_v$  is

$$\Delta H_v = a_4(\text{SA})^{1/2} + b_4(\sigma^2\nu)^{1/2} + c_4, \quad (4)$$

where  $a_4$  is 18.18689 kcal/mol-nm,  $b_4$  is 1.3321583 kcal/mol, and  $c_4$  is -16.142460 kcal/mol. The relationship for  $\Delta H_s$  is

$$\Delta H_s = a_5(SA)^2 + b_5(\sigma^2\nu)^{1/2} + c_5, \quad (5)$$

where  $a_5$  is 4.234303 kcal/mol-nm<sup>4</sup>,  $b_5$  is 2.5793785 kcal/mol, and  $c_5$  is -6.7335407 kcal/mol. (The temperature dependencies of the parameters are not predicted.)

### 2.3 Gas-Phase Proton and Methyl Cation Affinities of $\text{NO}_3^-$

Gutowski et al. (2005) derived  $\Delta H_I$  values (for a set of anions that are not considered in this study) from results obtained with a MP2/CBS model. In this study, the  $\Delta H_I$  values employed for  $\text{NO}_3^-$  were derived from experimental data reported in the open literature.

### 2.4 P/MCA Gas-Phase Proton and Methyl Cation Affinities

Gutowski et al. derived gas-phase proton and methyl cation affinities of P/MCAs from results obtained with a B3LYP/DZVP2 model. Results from the B3LYP/6-31+G(d,p) model were employed in this study. Results with the latter model were obtained for some of the species modeled by Gutowski et al. In accord with expectations, differences between the results are not significant.

### 2.5 Lattice Enthalpies

In the 2005 paper summarizing their method for obtaining  $\Delta G_r(298)$  values, Gutowski et al. derived estimates for lattice energies ( $U_L$ ) for 1:1 salts using a volume-based approach developed originally by Mallouk et al. (1984) and later refined by Jenkins and coworkers (Jenkins et al., 1999, 2002). The general form of the relationship is

$$U_L = 2I[\alpha/V^{1/3} + \beta], \quad (6)$$

where  $I$  is ionic strength (= 1 for the cases considered here),  $V$  is the molecular volume (which is the sum of the individual cation [ $V^+$ ] and anion [ $V^-$ ] molecular volumes in cubic nanometers), and  $\alpha$  and  $\beta$  are empirical constants. Lattice enthalpies [ $\Delta H_L(T)$ ] are then calculated based on the relationship

$$\Delta H_L(T) = U_L + RT[p(n_m/2 - 2) + q(n_x/2 - 2)], \quad (7)$$

where  $R$  is the universal gas constant,  $T$  is the temperature (298 K),  $p$  and  $q$  are 1 for 1:1 salts, and  $n_m$  and  $n_x$  are equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions. However, in a subsequent study, Gutowski and coworkers (2007) found for a set of well-characterized ammonium salts that  $\Delta H_L(T)$  estimates computed using the  $\alpha$  and  $\beta$  values recommended by Jenkins et al. did not agree well with values derived from experimental data. They therefore refit the model to an alternate set of data, obtaining  $\alpha = 19.9$  kcal-nm/mol and  $\beta = 37.6$  kcal/mol. Moreover, to get even better agreement, they scaled calculated ion-pair

volumes via an empirical equation, reducing them in proportion to their total calculated molecular volume. For the range of volumes considered in this study, these modifications yield  $\Delta H_L$  estimates whose magnitudes are 20–40 kcal/mol larger than those produced by the Jenkins model.

Basing  $V^+$ s and  $V^-$ s on the volume enclosed by an ion's 0.001 electron/bohr<sup>3</sup> surface, Gutowski et al. used B3LYP/DZVP2 results as the basis for calculating  $V^+$ s and B3LYP/aug-cc-pVDZ results as the basis for calculating  $V^-$ s. In this study, for salts with cations lacking nitroxy groups (uncorrected)  $V^+$ s obtained from B3LYP/6-31G(d,p) results were summed with a  $V^-$  value for the nitrate anion derived from measured data (Jenkins et al., 1999) to obtain  $V$ s. For salts with cations having nitroxy groups, the B3LYP/6-31G(d,p) model was coupled to a polarizable continuum model (Cossi et al., 2002) to obtain (model) geometries that the cations would acquire when solvated by water. Like water, salt crystals are polar media with dielectric constants  $>1$ , and the previous EQBR modeling study (McQuaid and Drake, 2010) showed that  $O^\alpha-N^\beta$  bond lengths produced by such calculations were in better agreement with results from crystallographic measurements than the  $O^\alpha-N^\beta$  bond length(s) produced by the (basic) B3LYP/6-31+G(d,p) model for an isolated gas-phase cation. For ammonium-functionalized cations, it was found that  $V^+$ s produced by the B3LYP/6-31G(d,p) model when it was not coupled to the PCM model were less than 1% larger, and differences in estimated  $\Delta H_L$  values were negligible.

The decision to use the B3LYP/6-31G(d,p) model for obtaining  $V^+$  estimates stemmed from consideration of a study by Byrd and Rice (2009). Using the B3LYP/6-31G(d,p) model to determine both  $V^+$ s and  $V^-$ s and adding a correction term that reduced  $V$ s in proportion to the number of H-atoms a salt had, they were able to get good density predictions for a wide range of energetic salts. Once such data was produced for this study, it was found that for most salts for which a measured density could be identified, the estimate produced by the Byrd-Rice model was too high. For salts with cations without N-H bonds, better overall agreement between measured and estimated densities was obtained when uncorrected  $V^+$ s were coupled with the  $V^-$  for  $\text{NO}_3$  that was derived from crystallographic data. Since obtaining good  $\Delta H_L$  estimates for salts with quaternized cations was our primary concern, that combination was used as input for equation 6 in all cases. (The development and validation of models with the potential to give better results for the entire range of salts considered here would have required more effort than could be justified.) Given the cube root dependence of  $\Delta U_L$  on molecular volume, from the standpoint of determining  $\Delta H_L$ , the differences in  $V$  predicted by the various models for a given cation should not be significant.

## 2.6 Entropic Energy Differences

As was done by Gutowski et al. (2005) estimated entropies ( $S$ ) of the P/MCA were calculated using a volume-based relationship developed for organic solids by Glasser and Jenkins (2004); namely,



$$S = a_8V + b_8, \quad (8)$$

where  $a_8 = 0.18499$  kcal/K-mol-nm<sup>3</sup> and  $b_8 = 0.01362$  kcal/K-mol. However, unlike Gutowski et al., who employed results from a B3LYP/DZVP2 model to estimate  $V$ , in this study, (uncorrected)  $V$  values calculated in the course of obtaining parameters to estimate  $\Delta H_v$  and  $\Delta H_s$  were employed instead. As discussed in section 2.2, those values were obtained from a B3LYP/6-31G(d) model. For HNO<sub>3</sub> and CH<sub>3</sub>NO<sub>3</sub>, measured standard entropies were employed. They are 63.7 cal/mol-K (Chase, 1998) and 75.9 cal/mol-K (Brand and Cawthon, 1955), respectively.

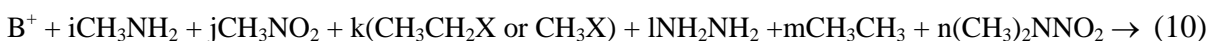
As was also done by Gutowski et al. (2005), entropies for the salts were calculated using a relationship developed by Glasser (2004); namely,

$$S = a_9(V^+ + V^-) + b_9, \quad (9)$$

where  $a_9 = 0.29792$  kcal/mol-nm<sup>3</sup>-K and  $b_9 = 0.00705$  kcal/mol-K. But in this study, (uncorrected) B3LYP/6-31G(d,p)-based determinations of  $V^+$  and measured  $V^-$  that were employed for estimating lattice energies were used as input. Gutowski et al. employed  $V_s$  obtained from a B3LYP/aug-cc-pVDZ model and later recommended that those values be scaled. From the standpoint of predicting thermal stabilities, the difference in  $T\Delta S$  energies derived from volumes obtained by the various models should not be significant.

## 2.7 Enthalpy of Formation Estimates

Enthalpy of formation [ $\Delta H_f(298)$ ] estimates for the salts were derived from (1) the estimation of gas-phase enthalpies of reaction for isodesmic schemes involving the cation of interest, (2) lattice enthalpies estimated per section 2.5, and (3)  $\Delta H_f(298)$  values derived from measured data. The isodesmic schemes had the general form



where X equals ONO<sub>2</sub> or OH. Data employed for these calculations are provided in the appendix.

## 3. Results

Together with figure 1, figures 3 and 4 depict all the cations and neutral molecules that were modeled in this study. Table 1 lists combinations of cations, P/MCAs, and P/MCDs for which  $\Delta G_r(298)$  values (for salt formation reactions) were calculated. In the subsections that follow, parameters calculated for each step of the B-H cycle employed to calculate  $\Delta G_r(298)$  values are presented and discussed separately.  $\Delta G_r(298)$ ,  $\rho$ , and  $\Delta H_f(298)$  values are then presented and discussed.

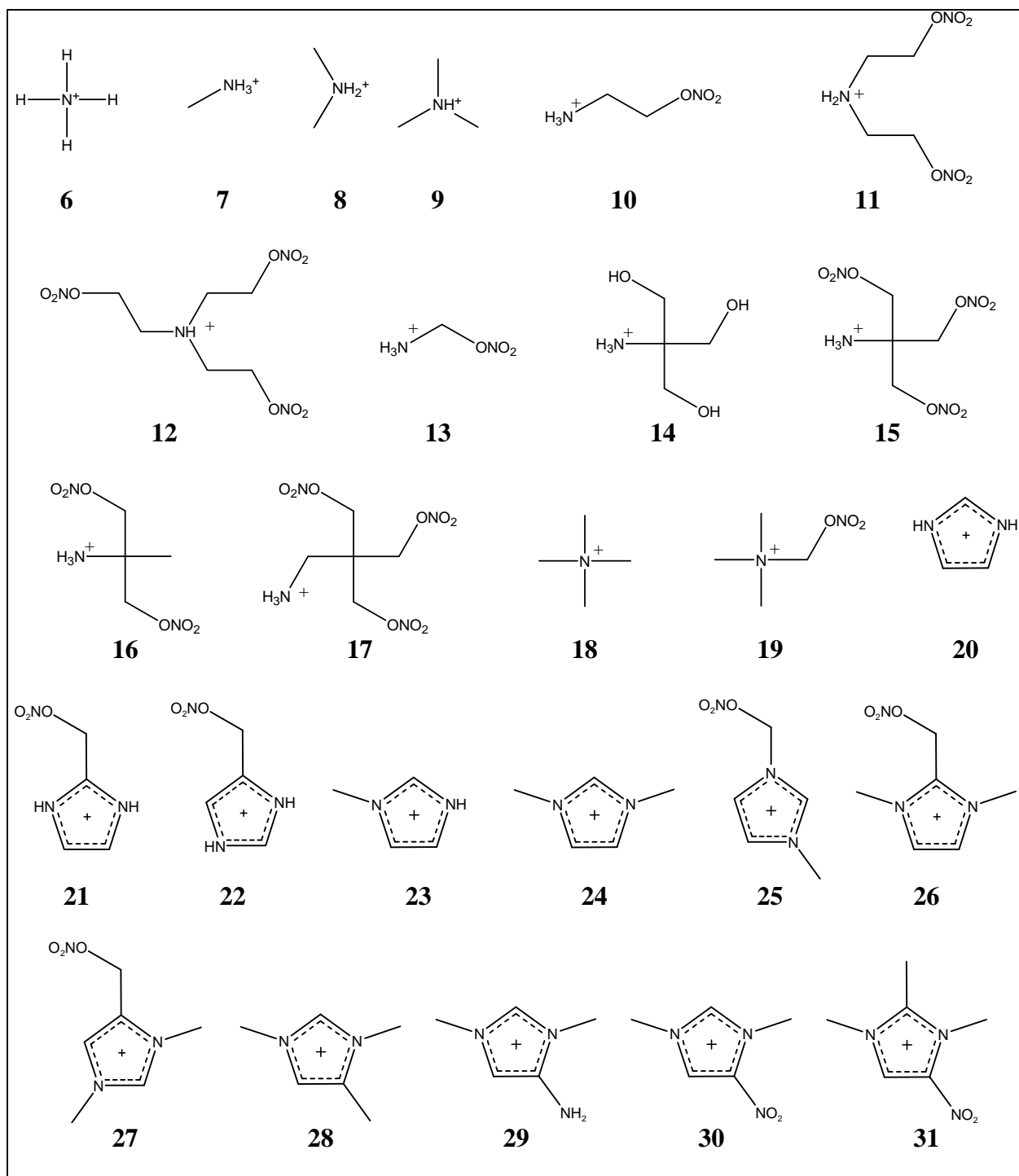


Figure 3. Cations characterized in this report.

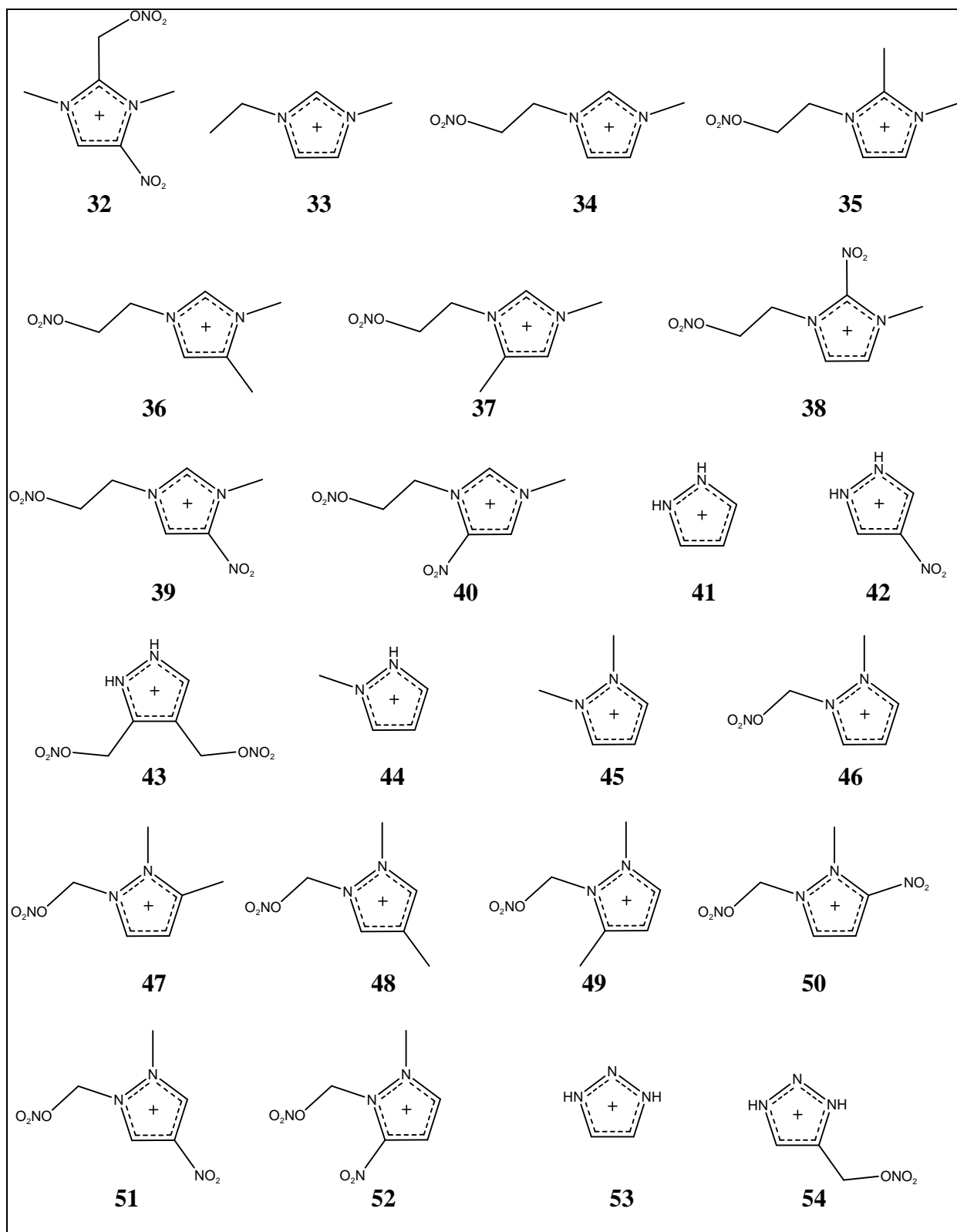


Figure 3. Cations characterized in this report (continued).

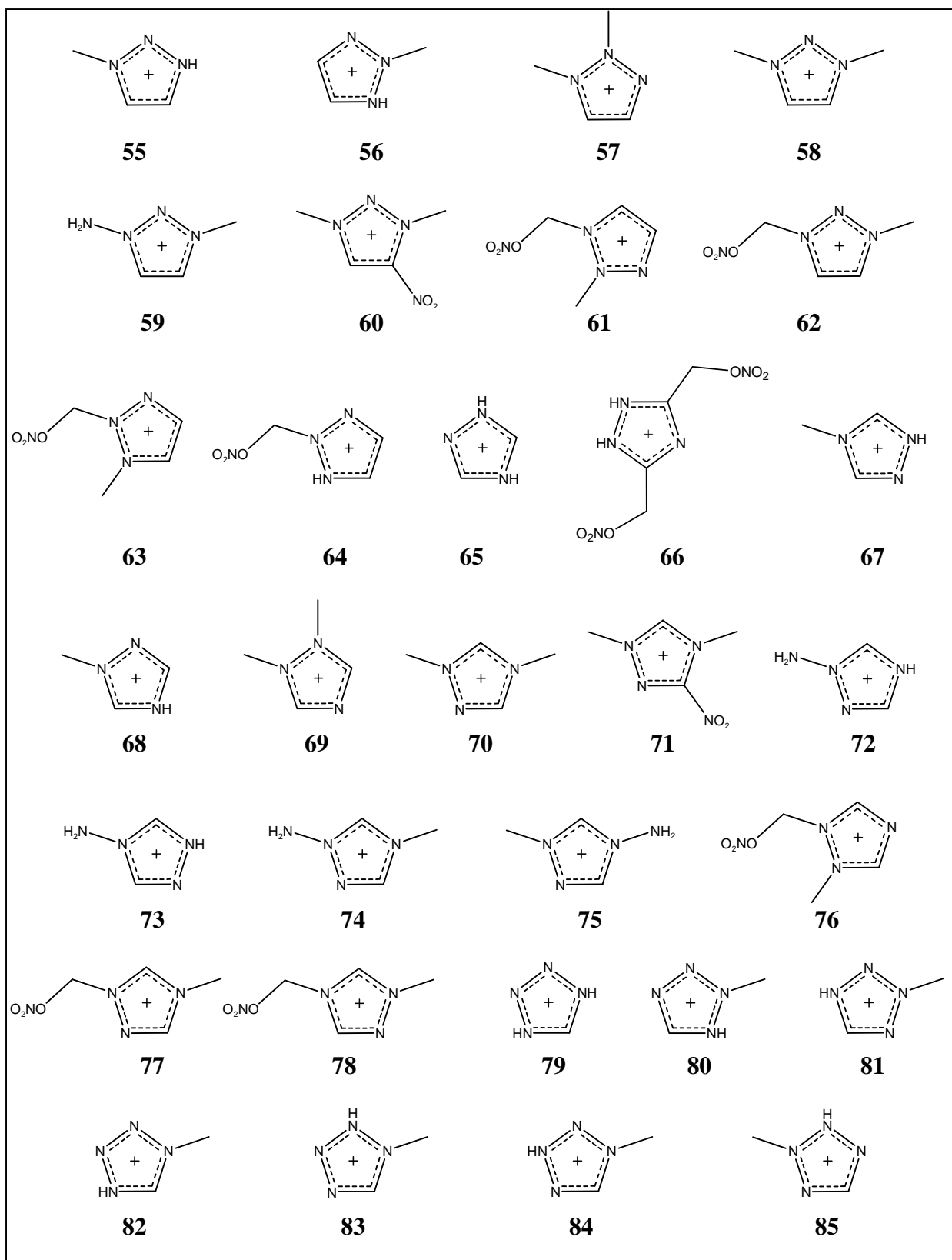


Figure 3. Cations characterized in this report (continued).

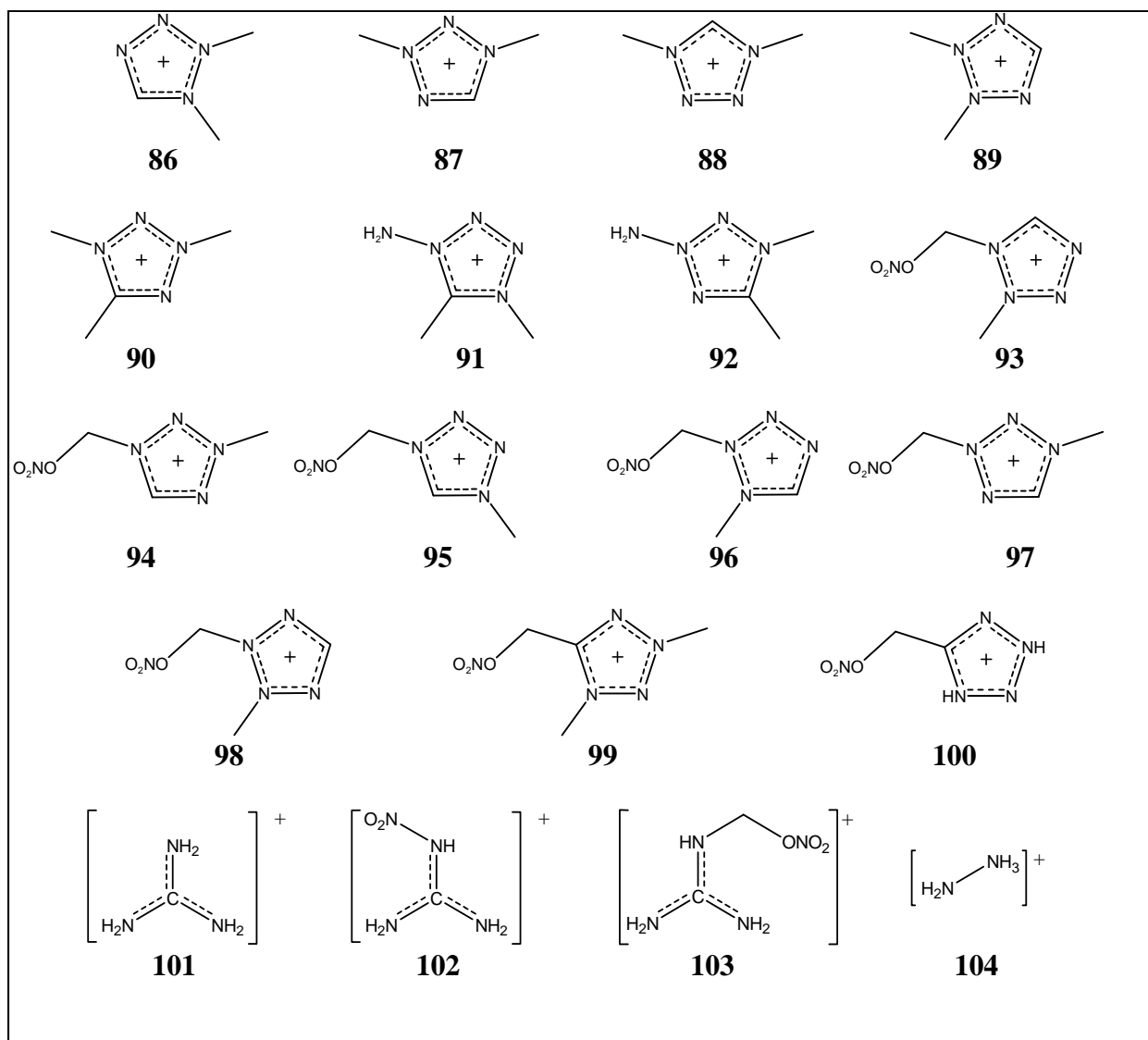


Figure 3. Cations characterized in this report (continued).

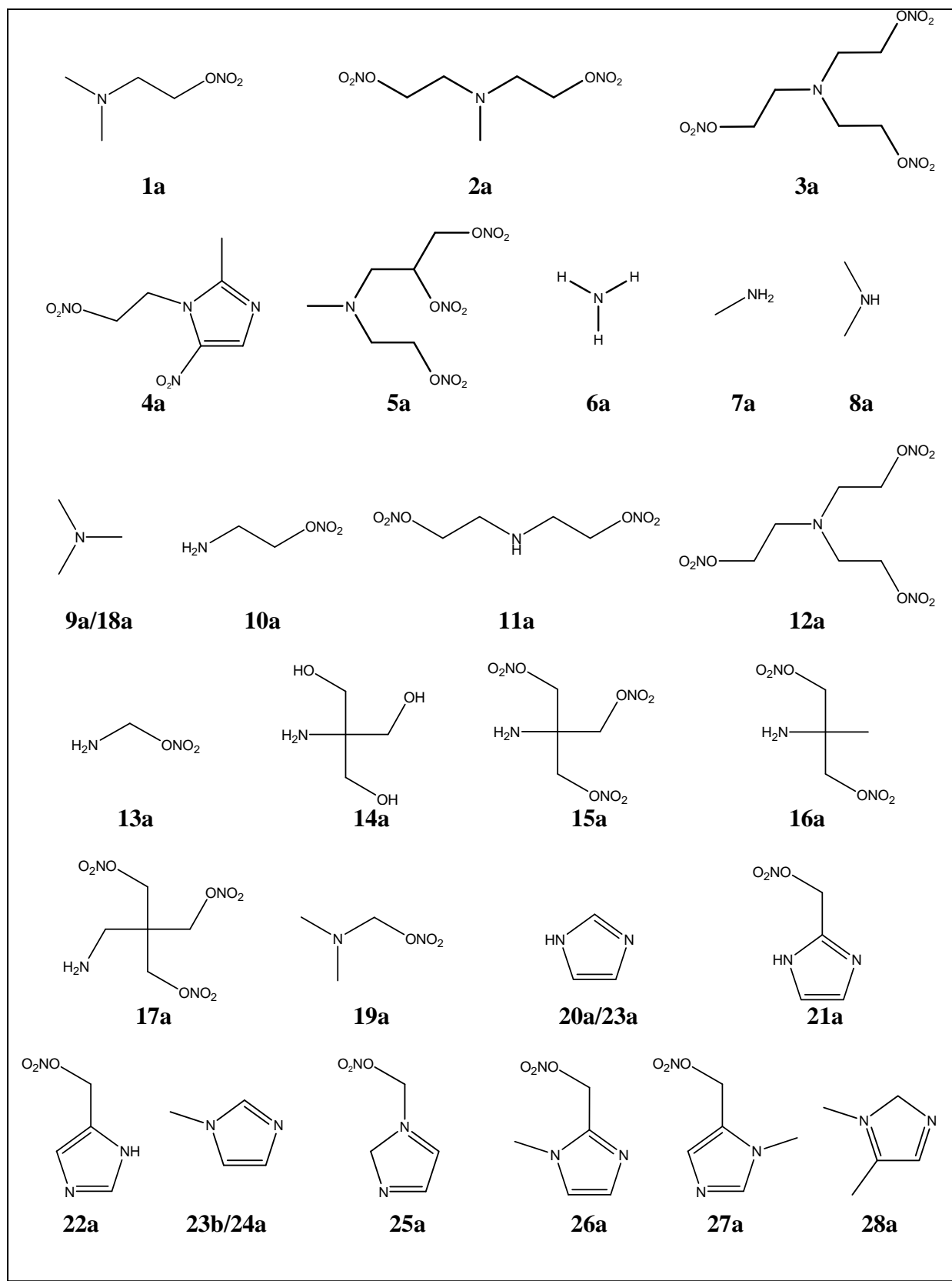


Figure 4. P/MCAs characterized in this report.

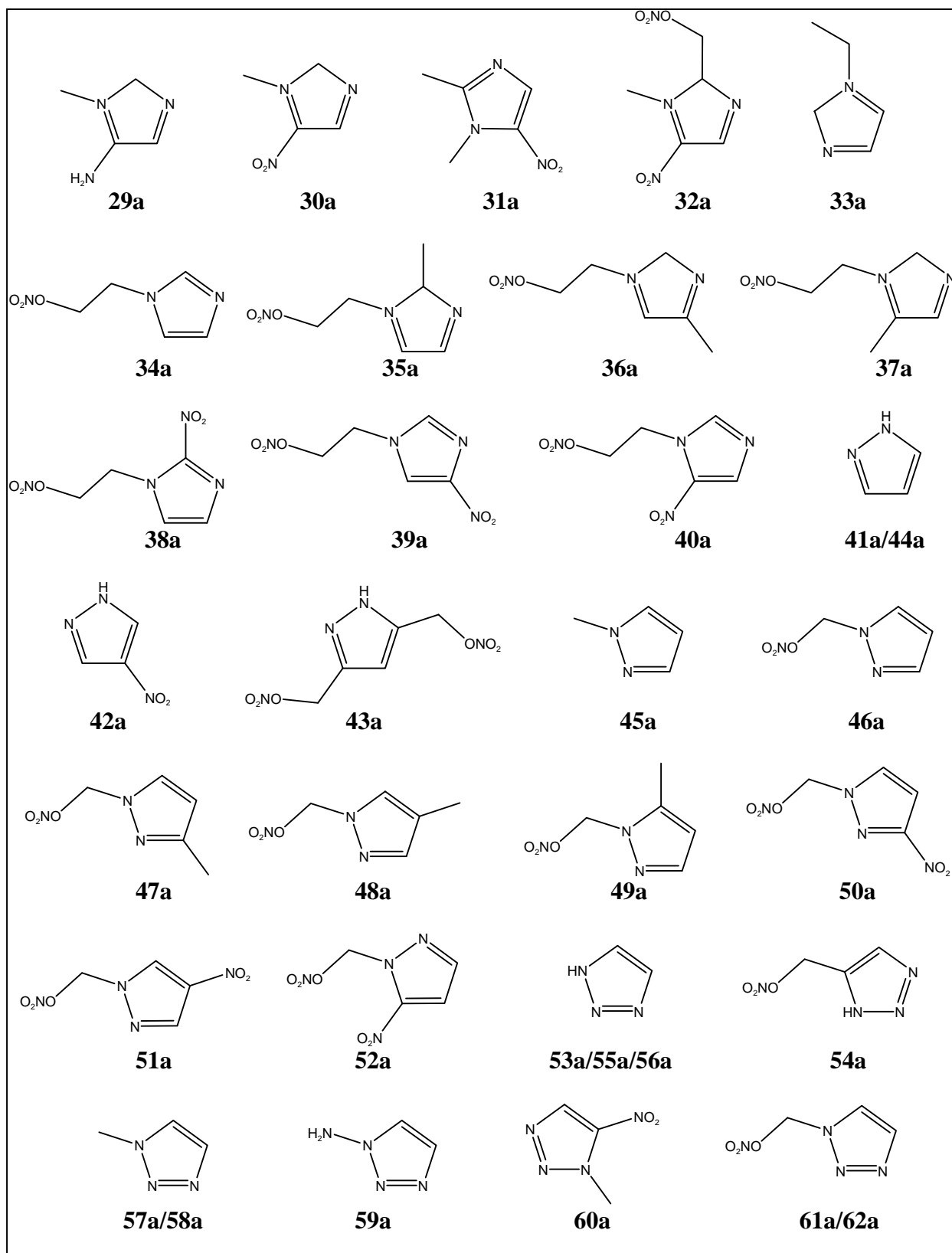


Figure 4. P/MCAs characterized in this report (continued).

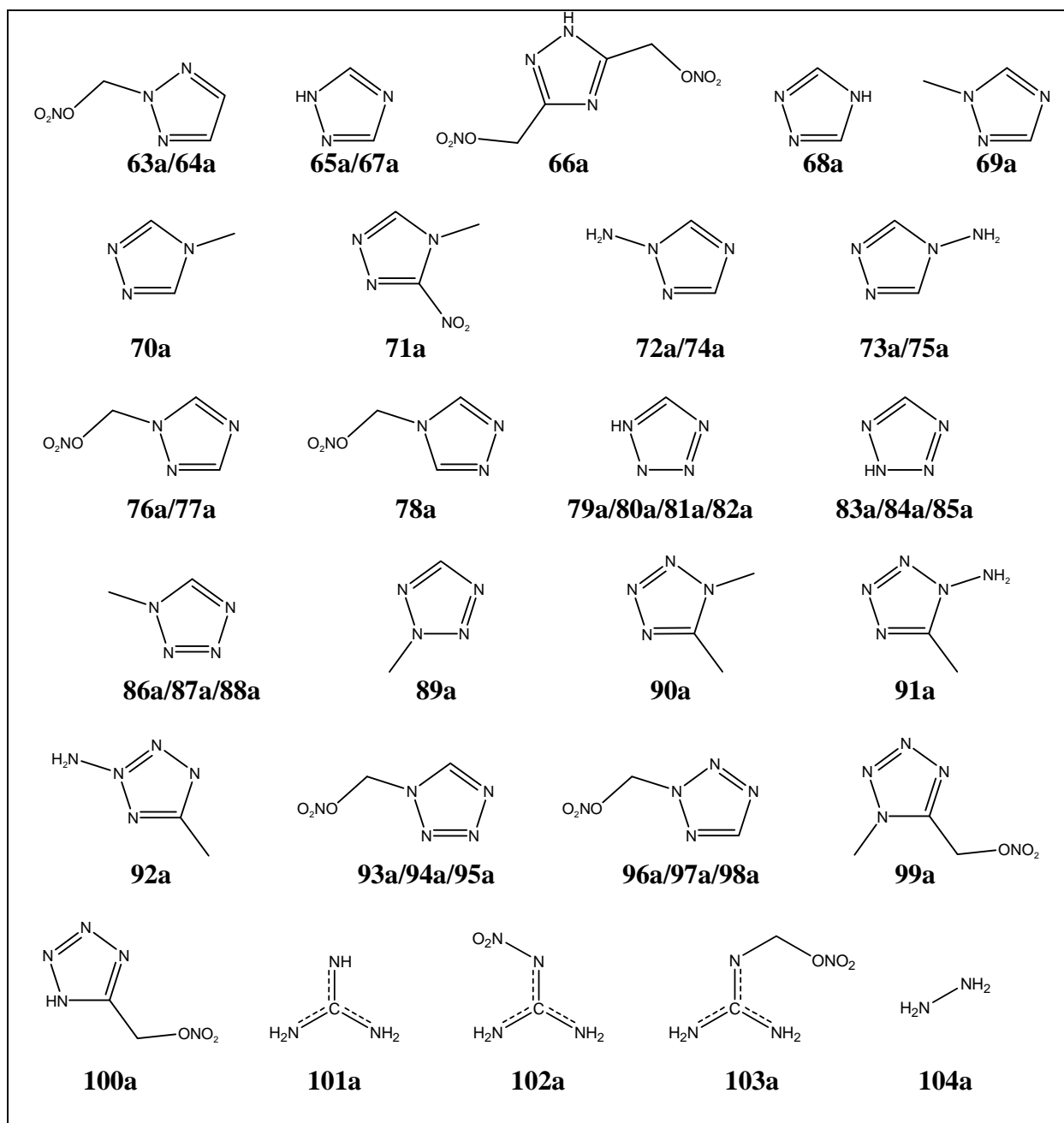


Figure 4. P/MCAs characterized in this report (continued).



Table 1. Combinations of cations, P/MCAs, and P/MCDs employed as bases for B-H cycle calculations.<sup>a</sup>

<b>Cation</b>	<b>P/MCA</b>	<b>P/MCD</b>
<b>Cations Synthesized by Drake et al. (2009)</b>		
2-nitroxy-N,N,N-trimethylethanam+ (1)	2-nitroxy-N,N-dimethylethanamine (1a)	CH <sub>3</sub> X
2-nitroxy-N-(2-nitroxyethyl)-N,N-dimethylethanam+ (2)	2-nitroxy-N-(2-nitroxyethyl)-N-methylethanamine (2a)	CH <sub>3</sub> X
2-nitroxy-N,N-bis(2-nitroxyethyl)-N-methylethanam+ (3)	2-nitroxy-N,N-bis(2-nitroxyethyl)ethanamine (3a)	CH <sub>3</sub> X
1-(2-nitroxyethyl)-2,3-dimethyl-5-nitroim+ (4)	1-(2-nitroxyethyl)-2-methyl-5-nitroimidazole (4a)	CH <sub>3</sub> X
2,3-dinitroxy-N-(2-nitroxyethyl)-N,N-dimethylpropanam+ (5)	2,3-dinitroxy-N-(2-nitroxyethyl)-N-methylpropanamine (5a)	CH <sub>3</sub> X
<b>Nonquaternary Ammonium Cations</b>		
ammonium (6)	ammonia (6a)	HX
methanam+ (7)	methanamine (7a)	HX
N-methylmethanam+ (8)	N-methylmethanamine (8a)	HX
N,N-dimethylmethanam+ (9)	N,N-dimethylmethanamine (9a/18a)	HX
2-nitroxyethanam+ (10)	2-nitroxyethanamine (10a)	HX
2-nitroxy-N-(2-nitroxyethyl)ethanam+ (11)	2-nitroxy-N-(2-nitroxyethyl)ethanamine (11a)	HX
2-nitroxy-N,N-bis(2-nitroxyethyl)ethanam+ (12)	2-nitroxy-N,N-bis(2-nitroxyethyl)ethanamine (12a)	HX
nitroxymethanam+ (13)	nitroxymethanamine (13a)	HX
Trizma [H <sub>3</sub> NC(CH <sub>2</sub> OH) <sub>3</sub> <sup>+</sup> ] (14)	2-amino-2-(hydroxymethyl)propanediol (14a)	HX
2-nitroxy-1,1-bis(nitroxymethyl)ethanam+ (15)	2-nitroxy-1,1-bis(nitroxymethyl)ethanamine (15a)	HX
2-nitroxy-1-nitroxymethyl-1methylethanam+ (16)	2-nitroxy-1-nitroxymethyl-1-methylethanamine (16a)	HX
3-nitroxy-2,2-bis(nitroxymethyl)propanam+ (17)	3-nitroxy-2,2-bis(nitroxymethyl)propanamine (17a)	HX
<b>Quaternary Ammonium Cations</b>		
tetramethylam+ (18)	N,N-dimethylmethanamine (9a/18a)	CH <sub>3</sub> X
nitroxy-N,N,N-trimethylmethanam+ (19)	nitroxy-N,N-dimethylmethamine (19a)	CH <sub>3</sub> X
<b>Imidazolium Cations</b>		
1,3H-imidazolium (20)	1H-imidazole (20a/23a)	HX
2-nitroxymethyl-1,3H-im+ (21)	2-nitroxymethyl-1H-imidazole (21a)	HX
4-nitroxymethyl-1,3H-im+ (22)	5-nitroxymethyl-1H-imidazole (22a)	HX
1-methyl-3H-im+ (23)	1H-imidazole (20a/23a)	CH <sub>3</sub> X

<sup>a</sup>am+ = ammonium, im+ = imidazolium, pyr+ = pyrazolium, triaz+ = triazolium, tetraz+ = tetrazolium, X = ONO<sub>2</sub>.

Table 1. Combinations of cations, P/MCAs, and P/MCDs employed as bases for B-H cycle calculations (continued).<sup>a</sup>

Cation	P/MCA	P/MCD
<b>Imidazolium Cations</b>		
1-methyl-3H-im+ (23)	1-methylimidazole (23b/24a)	HX
1,3-dimethylim+ (24)	1-methylimidazole (23b/24a)	CH <sub>3</sub> X
1-nitroxymethyl-3-methylim+ (25)	1-nitroxymethylimidazole (25a)	CH <sub>3</sub> X
1,3-dimethyl-2-nitroxymethylim+ (26)	1-methyl-2-nitroxymethylimidazole (26a)	CH <sub>3</sub> X
1,3-dimethyl-4-nitroxymethylim+ (27)	1-methyl-5-nitroxymethylimidazole (27a)	CH <sub>3</sub> X
1,3,4-trimethylim+ (28)	1,5-dimethylimidazole (28a)	CH <sub>3</sub> X
1,3-dimethyl-4-aminoim+ (29)	1-methyl-5-aminoimidazole (29a)	CH <sub>3</sub> X
1,3-dimethyl-4-nitroim+ (30)	1-methyl-5-nitroimidazole (30a)	CH <sub>3</sub> X
1,2,3-trimethyl-4-nitroim+ (31)	1,2-dimethyl-5-nitroimidazole (31a)	CH <sub>3</sub> X
1,3-dimethyl-2-nitroxymethyl-4-nitroim+ (32)	1-methyl-2-nitroxymethyl-5-nitroimidazole (32a)	CH <sub>3</sub> X
1-ethyl-3-methylim+ (33) (143314-14-1)	1-ethylimidazole (33a)	CH <sub>3</sub> X
1-(2-nitroxyethyl)-3-methylim+ (34)	1-(2-nitroxyethyl)imidazole (34a)	CH <sub>3</sub> X
1-(2-nitroxyethyl)-2,3-dimethylim+ (35)	1-(2-nitroxyethyl)-2-methylimidazole (35a)	CH <sub>3</sub> X
1-(2-nitroxyethyl)-3,4-dimethylim+ (36)	1-(2-nitroxyethyl)-4-methylimidazole (36a)	CH <sub>3</sub> X
1-(2-nitroxyethyl)-3,5-dimethylim+ (37)	1-(2-nitroxyethyl)-5-methylimidazole (37a)	CH <sub>3</sub> X
1-(2-nitroxyethyl)-3-methyl-2-nitroim+ (38)	1-(2-nitroxyethyl)-2-nitroimidazole (38a)	CH <sub>3</sub> X
1-(2-nitroxyethyl)-3-methyl-4-nitroim+ (39)	1-(2-nitroxyethyl)-4-nitroimidazole (39a)	CH <sub>3</sub> X
1-(2-nitroxyethyl)-3-methyl-5-nitroim+ (40)	1-(2-nitroxyethyl)-5-nitroimidazole (40a)	CH <sub>3</sub> X
<b>Pyrazolium Cations</b>		
1,2H-pyr+ (41)	1H-pyrazole (41a/44a)	HX
4-nitro-1,2H-pyr+ (42)	4-nitro-1H-pyrazole (42a)	HX
3,5-bis(nitroxymethyl)-1,2H-pyr+ (43)	3,5-bis(nitroxymethyl)-1H-pyrazole (43a)	HX
1-methyl-2H-pyr+ (44)	1H-pyrazole (41a/44a)	CH <sub>3</sub> X
1,2-dimethylpyr+ (45)	1-methylpyrazole (45a)	CH <sub>3</sub> X
1-nitroxymethyl-2-methylpyr+ (46)	1-nitroxymethylpyrazole (46a)	CH <sub>3</sub> X
1-nitroxymethyl-2,3-dimethylpyr+ (47)	1-nitroxymethyl-3-methylpyrazole (47a)	CH <sub>3</sub> X

<sup>a</sup>am+ = ammonium, im+ = imidazolium, pyr+ = pyrazolium, triaz+ = triazolium, tetraz+ = tetrazolium, X = ONO<sub>2</sub>.

Table 1. Combinations of cations, P/MCAs, and P/MCDs employed as bases for B-H cycle calculations (continued).<sup>a</sup>

Cation	P/MCA	P/MCD
<b>Pyrazolium Cations</b>		
1-nitroxymethyl-2,4-dimethylpyr+ (48)	1-nitroxymethyl-4-methylpyrazole (48a)	CH <sub>3</sub> X
1-nitroxymethyl-2,5-dimethylpyr+ (49)	1-nitroxymethyl-5-methylpyrazole (49a)	CH <sub>3</sub> X
1-nitroxymethyl-2-methyl-3-nitropyr+ (50)	1-nitroxymethyl-3-nitropyrazole (50a)	CH <sub>3</sub> X
1-nitroxymethyl-2-methyl-4-nitropyr+ (51)	1-nitroxymethyl-4-nitropyrazole (51a)	CH <sub>3</sub> X
1-nitroxymethyl-2-methyl-5-nitropyr+ (52)	1-nitroxymethyl-5-nitropyrazole (52a)	CH <sub>3</sub> X
<b>1,2,3-Triazolium Cations</b>		
1,3H-1,2,3-triaz+ (53)	1H-1,2,3-triazole (53a/55a/56a)	HX
4-nitroxymethyl-1,3H-1,2,3-triaz+ (54)	5-nitroxymethyl-1H-1,2,3-triazole (54a)	HX
1-methyl-3H-1,2,3-triaz+ (55)	1H-1,2,3-triazole (53a/55a/56a)	CH <sub>3</sub> X
2-methyl-1H-1,2,3-triaz+ (56)	1H-1,2,3-triazole (53a/55a/56a)	CH <sub>3</sub> X
1,2-dimethyl-1,2,3-triaz+ (57)	1-methyl-1,2,3-triazole (57a/58a)	CH <sub>3</sub> X
1,3-dimethyl-1,2,3-triaz+ (58)	1-methyl-1,2,3-triazole (57a/58a)	CH <sub>3</sub> X
1-amino-3-methyl-1,2,3-triaz+ (59)	1-amino-1,2,3-triazole (59a)	CH <sub>3</sub> X
1,3-dimethyl-4-nitro-1,2,3-triaz (60)	1-methyl-5-nitro-1,2,3-triazole (60a)	CH <sub>3</sub> X
1-nitroxymethyl-2-methyl-1,2,3-triaz+ (61)	1-nitroxymethyl-1,2,3-triazole (61a/62a)	CH <sub>3</sub> X
1-nitroxymethyl-3-methyl-1,2,3-triaz+ (62)	1-nitroxymethyl-1,2,3-triazole (61a/62a)	CH <sub>3</sub> X
1-methyl-2-nitroxymethyl-1,2,3-triaz+ (63)	2-nitroxymethyl-1,2,3-triazole (63a/64a)	CH <sub>3</sub> X
2-nitroxymethyl-1H-1,2,3-triaz+ (64)	2-nitroxymethyl-1,2,3-triazole (63a/64a)	HX
<b>1,2,4-Triazolium Cations</b>		
1,4H-1,2,4-triaz+ (65)	1H-1,2,4-triazole (65a/67a)	HX
3,5-bis(nitroxymethyl)-1,4H-1,2,4-triaz+ (66)	3,5-bis(nitroxymethyl)-1H-1,2,4-triazole (66a)	HX
4-methyl-1H-1,2,4-triaz+ (67)	1H-1,2,4-triazole (65a/67a)	CH <sub>3</sub> X
1-methyl-4H-1,2,4-triaz+ (68)	4H-1,2,4-triazole (68a)	CH <sub>3</sub> X
1,2-dimethyl-1,2,4-triaz+ (69)	1-methyl-1,2,4-triazole (69a)	CH <sub>3</sub> X
1,4-dimethyl-1,2,4-triaz+ (70)	4-methyl-1,2,4-triazole (70a)	CH <sub>3</sub> X

<sup>a</sup>am+ = ammonium, im+ = imidazolium, pyr+ = pyrazolium, triaz+ = triazolium, tetraz+ = tetrazolium, X = ONO<sub>2</sub>.

Table 1. Combinations of cations, P/MCAs, and P/MCDs employed as bases for B-H cycle calculations (continued).<sup>a</sup>

<b>Cation</b>	<b>P/MCA</b>	<b>P/MCD</b>
<b>1,2,4-Triazolium Cations</b>		
1,4-dimethyl-3-nitro-1,2,4-triaz+ (71)	4-methyl-3-nitro-1,2,4-triazole (71a)	CH <sub>3</sub> X
1-amino-4H-1,2,4-triaz+ (72)	1-amino-1,2,4-triazole (72a/74a)	HX
4-amino-1H-1,2,4-triaz+ (73)	4-amino-1,2,4-triazole (73a/75a)	HX
1-amino-4-methyl-1,2,4-triaz+ (74)	1-amino-1,2,4-triazole (72a/74a)	CH <sub>3</sub> X
1-methyl-4-amino-1,2,4-triaz+ (75)	4-amino-1,2,4-triazole (73a/75a)	CH <sub>3</sub> X
1-nitroxymethyl-2-methyl-1,2,4-triaz+ (76)	1-nitroxymethyl-1,2,4-triazole (76a/77a)	CH <sub>3</sub> X
1-nitroxymethyl-4-methyl-1,2,4-triaz+ (77)	1-nitroxymethyl-1,2,4-triazole (76a/77a)	CH <sub>3</sub> X
1-methyl-4-nitroxymethyl-1,2,4-triaz+ (78)	4-nitroxymethyl-1,2,4-triazole (78a)	CH <sub>3</sub> X
<b>Tetrazolium Cations</b>		
1,4H-tetraz+ (79)	1H-tetrazole (79a/80a/81a/82a)	HX
2-methyl-1H-tetraz+ (80)	1H-tetrazole (79a/80a/81a/82a)	CH <sub>3</sub> X
3-methyl-1H-tetraz+ (81)	1H-tetrazole (79a/80a/81a/82a)	CH <sub>3</sub> X
1-methyl-4H-tetraz+ (82)	1H-tetrazole (79a/80a/81a/82a)	CH <sub>3</sub> X
1-methyl-2H-tetraz+ (83)	2H-tetrazole (83a/84a/85a)	CH <sub>3</sub> X
1-methyl-3H-tetraz+ (84)	2H-tetrazole (83a/84a/85a)	CH <sub>3</sub> X
2-methyl-3H-tetraz+ (85)	2H-tetrazole (83a/84a/85a)	CH <sub>3</sub> X
1,2-dimethyltetraz+ (86)	1-methyltetrazole (86a/87a/88a)	CH <sub>3</sub> X
1,3-dimethyltetraz+ (87)	1-methyltetrazole (86a/87a/88a)	CH <sub>3</sub> X
1,4-dimethyltetraz+ (88)	1-methyltetrazole (86a/87a/88a)	CH <sub>3</sub> X
2,3-dimethyltetraz+ (89)	2-methyltetrazole (89a)	CH <sub>3</sub> X
1,3,5-trimethyltetraz+ (90)	1,5-dimethyltetrazole (90a)	CH <sub>3</sub> X
1-amino-4,5-dimethyltetraz+ (91)	1-amino-5-methyltetrazole (91a)	CH <sub>3</sub> X
1,5-dimethyl-3-aminotetraz+ (92)	2-amino-5-methyltetrazole (92a)	CH <sub>3</sub> X
1-nitroxymethyl-2-methyltetraz+ (93)	1-nitroxymethyltetrazole (93a/94a/95a)	CH <sub>3</sub> X
1-nitroxymethyl-3-methyltetraz+ (94)	1-nitroxymethyltetrazole (93a/94a/95a)	CH <sub>3</sub> X

<sup>a</sup>am+ = ammonium, im+ = imidazolium, pyr+ = pyrazolium, triaz+ = triazolium, tetraz+ = tetrazolium, X = ONO<sub>2</sub>.

Table 1. Combinations of cations, P/MCAs, and P/MCDs employed as bases for B-H cycle calculations (continued).<sup>a</sup>

<b>Cation</b>	<b>P/MCA</b>	<b>P/MCD</b>
<b>Tetrazolium Cations</b>		
1-nitroxymethyl-4-methyltetraz+ (95)	1-nitroxymethyltetrazole (93a/94a/95a)	CH <sub>3</sub> X
1-methyl-2-nitroxymethyltetraz+ (96)	2-nitroxymethyltetrazole (96a/97a/98a)	CH <sub>3</sub> X
1-methyl-3-nitroxymethyltetraz+ (97)	2-nitroxymethyltetrazole (96a/97a/98a)	CH <sub>3</sub> X
2-nitroxymethyl-3-methyltetraz+ (98)	2-nitroxymethyltetrazole (96a/97a/98a)	CH <sub>3</sub> X
1,3-dimethyl-5-nitroxymethyltetraz+ (99)	1-methyl-5-nitroxymethyltetrazole (99a)	CH <sub>3</sub> X
5-nitroxymethyl-1,3H-tetraz+ (100)	5-nitroxymethyl-1H-tetrazole (100a)	HX
<b>Guanidinium and Hydrazinium Cations</b>		
guanidinium (101)	guanidine (101a)	HX
1-nitro-1H-guanidinium (102)	nitroguanidine (102a)	HX
nitroxymethylguanidinium (103)	nitroxymethylguanidine (103a)	HX
hydrazinium (104)	hydrazine (104a)	HX

<sup>a</sup>am+ = ammonium, im+ = imidazolium, pyr+ = pyrazolium, triaz+ = triazolium, tetraz+ = tetrazolium, X = ONO<sub>2</sub>.

### 3.1 Enthalpy of Vaporization and Enthalpy of Sublimation Estimates

Table 2 presents  $V$ ,  $SA$ ,  $\nu$ , and  $\sigma^2$  values determined for the 0.001 atomic unit (au) surfaces of neutral molecules modeled in this study. The table also includes  $\Delta H_v$  and  $\Delta H_s$  estimates derived from equations 4 and 5. Measured  $\Delta H_v$  and  $\Delta H_s$  values that were found in the open literature are included for comparison. In all but one case, estimates are within 5 kcal/mol of their corresponding measured value. The exception is the  $\Delta H_v$  estimate for 1,5-dimethyltetrazole. However, 1,5-dimethyltetrazole has a melting point near 298 K, so the  $\Delta H_s$  estimate, which is within 4 kcal/mol of the measured enthalpy of the phase change, could be considered a more appropriate parameter for comparison. Gutowski et al. (2005) reported a single nominal “enthalpy of vaporization” estimate for “imidizoles” that was the average of estimates calculated for imidazole, 1-, 2-, and 5-methylimidazole, and 1,2-, 1,4-, and 1,5-dimethylimidazole. That value (10.6 kcal/mol) is less than the  $\Delta H_v$  and  $\Delta H_s$  estimates for imidazole, 1-methylimidazole, 1,5-dimethylimidazole, and 1-ethylimidazole that were calculated in this study.

The substitution of various functional groups for H-atoms on a given cationic platform lead to relatively systematic changes in  $SA$ ,  $\nu$ , and  $\sigma^2$ , and therefore to systematic differences in  $\Delta H_s$  and  $\Delta H_v$ . Differences between the results for 1H-imidazole, 1-methylimidazole, 1-ethylimidazole, and 1-(2-nitroxyethyl) imidazole are representative of the types of changes observed. The substitution of a methyl group for the H-atom bonded to the N-atom at the ring’s 1-position produces a molecule (1-methylimidazole) with a 0.22 nm<sup>2</sup> larger 0.001 au  $SA$ , but with significantly lower  $\nu$  and  $\sigma^2$  values. Together, those changes produce (through equations 2 and 3, respectively)  $\Delta H_s$  and  $\Delta H_v$  estimates for 1-methylimidazole that are lower than those of 1H-imidazole. The substitution of a methyl group for one of the H-atoms on the methyl group at the 1-position of 1-methylimidazole also produces a molecule (1-ethylimidazole) with a 0.22 nm<sup>2</sup> larger  $SA$  value. But in this case,  $\nu$  and  $\sigma^2$  remain relatively unchanged. As a result, the  $\Delta H_s$  and  $\Delta H_v$  estimates for 1-ethylimidazole are slightly larger than those for 1-methylimidazole. Finally, the substitution of a nitroxy group for one of the H-atoms at the 2-position of the ethyl chain of 1-ethylimidazole produces a molecule [1-(2-nitroxyethyl)imidazole] that has a 0.39 nm<sup>2</sup> larger  $SA$  value and a significantly larger  $\nu$  value as well. With  $\sigma^2$  being about the same in both cases, it leads to  $\Delta H_v$  and  $\Delta H_s$  estimates for 1-(2-nitroxyethyl)imidazole that are significantly higher than those calculated for 1-ethylimidazole.

The results in table 2 indicate that substitution of methyl, amino, nitro and nitroxy groups for H-atoms bonded to C-atoms invariably lead to increases in  $\Delta H_v$  and  $\Delta H_s$ . Since higher  $\Delta H_v$  and  $\Delta H_s$  values lead to more positive/less negative  $\Delta G_r(298)$  values, the equilibrium (constant) will be shifted toward the neutrals unless a concomitant change in another parameter in the B-H cycle counteracts the effect.

Table 2. Properties associated with the 0.001 electron/bohr<sup>3</sup> surface of (neutral) P/MCAs, estimates for  $\Delta H_v$  and  $\Delta H_s$ , and comparisons to alternately derived values.<sup>a</sup>

	$V$ nm <sup>3</sup>	$SA$ nm <sup>2</sup>	$\nu$	$\sigma^2$	$\Delta H_v$		$\Delta H_s$	
					b	Other	b	Other
<b>P/MCA Paired With Cations 1-5</b>								
2-nitroxy-N,N-dimethylethanamine	0.169	1.779	0.186	59.5	12.5	—	15.2	—
2-nitroxy-N-(2-nitroxyethyl)-N-methylethanamine	0.231	2.313	0.250	80.2	17.5	—	27.5	—
2-nitroxy-N,N-bis(2-nitroxyethyl)ethanamine	0.294	2.901	0.222	80.9	20.5	—	39.8	—
1-(2-nitroxyethyl)-2-methyl-5-nitroimidazole	0.226	2.230	0.243	142.5	18.9	—	29.5	—
2,3-dinitroxy-N-(2-nitroxyethyl)-N-methylpropanamine	0.295	2.925	0.228	90.4	21.0	—	41.2	—
<b>Amines</b>								
ammonia (g) (7664-41-7)	0.034	0.513	0.131	229.5	—	—	—	—
methanamine (g) (74-89-5)	0.058	0.766	0.148	222.8	—	—	—	—
N-methylmethanamine (l) (124-40-3)	0.082	0.990	0.122	160.6	7.9	6.1 <sup>c</sup>	—	—
N,N-dimethylmethanamine (g) (75-50-3)	0.106	1.180	0.043	109.2	—	—	—	—
2-nitroxyethanamine	0.121	1.375	0.248	95.8	11.7	—	13.8	—
2-nitroxy-N-(2-nitroxyethyl)ethanamine	0.209	2.201	0.245	89.8	17.1	—	25.9	—
2-nitroxy-N,N-bis(2-nitroxyethyl)ethanamine	0.294	2.905	0.209	110.2	21.3	—	41.4	—
nitroxymethanamine	0.098	1.145	0.233	153.8	11.3	—	14.2	—
2-amino-2-(hydroxymethyl)propanediol (s) (77-86-1)	0.153	1.539	0.250	224.1	16.4	—	22.6	—
2-nitroxy-1,1-bis(nitroxymethyl)ethanamine	0.246	2.484	0.142	112.4	17.8	—	29.7	—
2-nitroxy-1-nitroxymethyl-1-methylethanamine	0.206	2.102	0.223	87.9	16.1	—	23.4	—
3-nitroxy-2,2-bis(nitroxymethyl)propanamine	0.268	2.637	0.178	119.2	19.5	—	34.6	—
nitroxy-N,N-dimethylmethanamine	0.145	1.538	0.198	76.1	11.6	—	13.3	—

<sup>a</sup>If known, the state of the compound at 298 K and 1 atm is provided. <sup>b</sup>Present work. <sup>c</sup>Majer and Svoboda, 1985. <sup>d</sup>Measured value for 293–309 K (Jimenez et al., 1987).

<sup>e</sup>The hydroxy-functionalized analog (CAS no. 3724-26-3) has been synthesized and is a liquid (Jones, 1949). <sup>f</sup>The hydroxy-functionalized analog (CAS no. 822-55-9) has

been synthesized. <sup>g</sup>Average of estimates calculated for imidazole and mono- and di-methyl-substituted imidazoles (Gutowski et al., 2005). <sup>h</sup>The hydroxy-functionalized

analog (CAS no. 17334-08-6) has been synthesized and is a solid (Jocelyn, 1957). <sup>i</sup>The hydroxy-functionalized analog (CAS no. 38993-84-9) has been synthesized and is

a solid (Martin et al., 1968). <sup>j</sup>Martin et al., 1968. <sup>k</sup>Xue et al., 2005. <sup>l</sup>The hydroxy-functionalized analog (CAS no. 936-05-0) has been synthesized (Rufer et al., 1971).

<sup>m</sup>Measured value for 268–287 K (Jimenez et al., 1987). <sup>n</sup>Katritzky et al., 2007. <sup>o</sup>The hydroxy-functionalized analog has been synthesized and is a solid (Llamas-Saiz et

al., 1992). <sup>p</sup>The hydroxy-functionalized analog (CAS no. 84440-19-7) has been synthesized and is a solid (Banert, 1989). <sup>q</sup>The hydroxy-functionalized analog (CAS no.

78910-04-0) has been synthesized and is a solid (Machin et al., 1984). <sup>r</sup>Jimenez et al., 1989. <sup>s</sup>The hydroxy-functionalized analog (CAS no. 22250-36-8) has been

synthesized and is a solid (Norikov et al., 1969). <sup>t</sup>ChemSpider Web site, 2010. <sup>u</sup>Sukhanov et al., 2005. <sup>v</sup>Xue et al., 2004. <sup>w</sup>Kabo et al., 1993. <sup>x</sup>Kozyro et al., 1990.

<sup>y</sup>Measured value for 402–473 K (Cundall et al., 1978). <sup>z</sup>Schmidt, 2001.

Table 2. Properties associated with the 0.001 electron/bohr<sup>3</sup> surface of (neutral) P/MCAs, estimates for  $\Delta H_v$  and  $\Delta H_s$ , and comparisons to alternately derived values (continued).<sup>a</sup>

	$V$ nm <sup>3</sup>	$SA$ nm <sup>2</sup>	$\nu$	$\sigma^2$	$\Delta H_v$		$\Delta H_s$	
					b	Other	b	Other
<b>Imidazoles</b>								
1H-imidazole ( <i>s</i> ) (288-32-4)	0.089	1.031	0.250	329.5	14.4	—	21.2	19.8 <sup>d</sup>
2-nitroxymethyl-1H-imidazole <sup>e</sup>	0.153	1.655	0.216	209.5	16.2	—	22.2	—
5-nitroxymethyl-1H-imidazole <sup>f</sup>	0.153	1.656	0.222	229.8	16.8	—	23.3	—
1-methylimidazole ( <i>l</i> ) (616-47-7)	0.113	1.255	0.160	208.5	11.9	10.6 <sup>g</sup>	14.8	—
1-nitroxymethylimidazole	0.154	1.660	0.244	182.3	16.2	—	22.1	—
1-methyl-2-nitroxymethylimidazole <sup>h</sup>	0.176	1.836	0.249	135.7	16.3	—	22.6	—
1-methyl-5-nitroxymethylimidazole <sup>i</sup>	0.176	1.836	0.245	141.4	16.3	—	22.7	—
1,5-dimethylimidazole ( <i>l</i> ) <sup>j</sup> (10447-93-5)	0.136	1.448	0.131	224.7	13.0	10.6 <sup>g</sup>	16.2	—
1-methyl-5-aminoimidazole ( <i>s</i> ) (66787-75-5)	0.128	1.389	0.191	240.8	14.3	—	19.0	—
1-methyl-5-nitroimidazole ( <i>s</i> ) <sup>k</sup> (443-48-1)	0.140	1.489	0.250	163.8	14.6	—	19.1	—
1,2-dimethyl-5-nitroimidazole ( <i>s</i> ) <sup>k</sup>	0.163	1.679	0.232	153.9	15.4	—	20.6	—
1-methyl-2-nitroxymethyl-5-nitroimidazole <sup>l</sup>	0.203	2.075	0.232	135.3	17.5	—	26.0	—
1-ethylimidazole ( <i>l</i> ) (7098-07-9)	0.136	1.463	0.129	209.9	12.8	—	15.8	—
1-(2-nitroxyethyl)imidazole	0.177	1.850	0.250	206.6	18.2	—	26.3	—
1-(2-nitroxyethyl)-2-methylimidazole	0.199	2.018	0.250	207.0	19.3	—	29.1	—
1-(2-nitroxyethyl)-4-methylimidazole	0.200	2.076	0.250	209.1	19.7	—	30.2	—
1-(2-nitroxyethyl)-5-methylimidazole	0.199	2.030	0.240	190.7	18.8	—	28.2	—
1-(2-nitroxyethyl)-2-nitroimidazole	0.204	2.072	0.248	187.5	19.1	—	29.0	—
1-(2-nitroxyethyl)-4-nitroimidazole	0.206	2.129	0.247	313.9	22.1	—	35.2	—
1-(2-nitroxyethyl)-5-nitroimidazole	0.204	2.070	0.224	157.1	17.9	—	26.7	—

<sup>a</sup>If known, the state of the compound at 298 K and 1 atm is provided. <sup>b</sup>Present work. <sup>c</sup>Majer and Svoboda, 1985. <sup>d</sup>Measured value for 293–309 K (Jimenez et al., 1987). <sup>e</sup>The hydroxy-functionalized analog (CAS no. 3724-26-3) has been synthesized and is a liquid (Jones, 1949). <sup>f</sup>The hydroxy-functionalized analog (CAS no. 822-55-9) has been synthesized. <sup>g</sup>Average of estimates calculated for imidazole and mono- and di-methyl-substituted imidazoles (Gutowski et al., 2005). <sup>h</sup>The hydroxy-functionalized analog (CAS no. 17334-08-6) has been synthesized and is a solid (Jocelyn, 1957). <sup>i</sup>The hydroxy-functionalized analog (CAS no. 38993-84-9) has been synthesized and is a solid (Martin et al., 1968). <sup>j</sup>Martin et al., 1968. <sup>k</sup>Xue et al., 2005. <sup>l</sup>The hydroxy-functionalized analog (CAS no. 936-05-0) has been synthesized (Rufer et al., 1971). <sup>m</sup>Measured value for 268–287 K (Jimenez et al., 1987). <sup>n</sup>Katritzky et al., 2007. <sup>o</sup>The hydroxy-functionalized analog has been synthesized and is a solid (Llamas-Saiz et al., 1992). <sup>p</sup>The hydroxy-functionalized analog (CAS no. 84440-19-7) has been synthesized and is a solid (Banert, 1989). <sup>q</sup>The hydroxy-functionalized analog (CAS no. 78910-04-0) has been synthesized and is a solid (Machin et al., 1984). <sup>r</sup>Jimenez et al., 1989. <sup>s</sup>The hydroxy-functionalized analog (CAS no. 22250-36-8) has been synthesized and is a solid (Norikov et al., 1969). <sup>t</sup>ChemSpider Web site, 2010. <sup>u</sup>Sukhanov et al., 2005. <sup>v</sup>Xue et al., 2004. <sup>w</sup>Kabo et al., 1993. <sup>x</sup>Kozyro et al., 1990. <sup>y</sup>Measured value for 402–473 K (Cundall et al., 1978). <sup>z</sup>Schmidt, 2001.



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	$V$ nm <sup>3</sup>	$SA$ nm <sup>2</sup>	$\nu$	$\sigma^2$	$\Delta H_v$		$\Delta H_s$	
					b	Other	b	Other
<b>Pyrazoles</b>								
1H-pyrazole ( <i>s</i> ) (288-13-1)	0.089	1.031	0.247	233.7	12.5	—	17.4	17.4 <sup>m</sup>
4-nitro-1H-pyrazole ( <i>s</i> ) <sup>n</sup> (2075-46-9)	0.118	1.307	0.183	327.1	15.0	—	20.5	—
3,5-bis(nitroxymethyl)-1H-pyrazole <sup>o</sup>	0.217	2.283	0.176	171.7	18.7	—	29.5	—
1-methylpyrazole ( <i>l</i> ) (930-36-9)	0.113	1.258	0.188	138.4	11.0	—	13.1	—
1-(nitroxymethyl)pyrazole	0.154	1.647	0.249	135.1	14.9	—	19.7	—
1-nitroxymethyl-3-methylpyrazole	0.177	1.871	0.250	133.8	16.4	—	23.0	—
1-nitroxymethyl-4-methylpyrazole	0.177	1.872	0.248	123.3	16.1	—	22.4	—
1-nitroxymethyl-5-methylpyrazole	0.176	1.827	0.243	116.0	15.5	—	21.1	—
1-nitroxymethyl-3-nitropyrazole	0.183	1.927	0.242	221.2	18.9	—	27.9	—
1-nitroxymethyl-4-nitropyrazole	0.183	1.925	0.217	193.6	17.7	—	25.7	—
1-nitroxymethyl-5-nitropyrazole	0.182	1.878	0.228	101.4	15.2	—	20.6	—
<b>1,2,3-Triazoles</b>								
1H-1,2,3-triazole ( <i>l</i> , mp =296 K) (288-36-8)	0.084	0.982	0.249	355.0	14.4	—	21.6	—
5-nitroxymethyl-1H-1,2,3-triazole <sup>p</sup>	0.148	1.610	0.230	269.0	17.4	—	24.5	—
1-methyl-1,2,3-triazole ( <i>l</i> ) (16681-65-5)	0.107	1.210	0.175	232.2	12.4	—	15.9	—
1-amino-1,2,3-triazole ( <i>s</i> ) (584-14-5)	0.101	1.150	0.250	367.4	16.1	—	23.6	—
1-methyl-5-nitro-1,2,3-triazole	0.136	1.453	0.249	181.0	12.7	—	15.6	—
1-nitroxymethyl-1,2,3-triazole	0.148	1.617	0.241	198.0	16.2	—	22.2	—
2-nitroxymethyl-1,2,3-triazole <sup>q</sup>	0.148	1.618	0.232	97.4	13.3	—	16.6	—

<sup>a</sup>If known, the state of the compound at 298 K and 1 atm is provided. <sup>b</sup>Present work. <sup>c</sup>Majer and Svoboda, 1985. <sup>d</sup>Measured value for 293–309 K (Jimenez et al., 1987).

<sup>e</sup>The hydroxy-functionalized analog (CAS no. 3724-26-3) has been synthesized and is a liquid (Jones, 1949). <sup>f</sup>The hydroxy-functionalized analog (CAS no. 822-55-9) has

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<sup>m</sup>Measured value for 268–287 K (Jimenez et al., 1987). <sup>n</sup>Katritzky et al., 2007. <sup>o</sup>The hydroxy-functionalized analog has been synthesized and is a solid (Llamas-Saiz et

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	$V$ nm <sup>3</sup>	$SA$ nm <sup>2</sup>	$\nu$	$\sigma^2$	$\Delta H_v$		$\Delta H_s$	
					b	Other	b	Other
<b>1,2,4-Triazoles</b>								
1H-1,2,4-triazole ( <i>s</i> ) (288-88-0)	0.083	0.978	0.225	316.9	13.1	—	19.1	20.1 <sup>f</sup>
3,5-bis(nitroxymethyl)-1H-1,2,4-triazole <sup>s</sup>	0.211	2.234	0.175	183.5	18.6	—	29.0	—
4H-1,2,4-triazole ( <i>s</i> ) (37306-44-8)	0.083	0.981	0.250	429.9	15.7	—	24.1	—
1-methyl-1,2,4-triazole ( <i>l</i> , mp = 289 K) <sup>l</sup> (6086-21-1)	0.107	1.206	0.218	174.4	12.0	—	15.3	—
4-methyl-1,2,4-triazole ( <i>s</i> ) (10570-40-8)	0.107	1.208	0.169	289.4	13.2	—	17.5	—
4-methyl-3-nitro-1,2,4-triazole ( <i>s</i> ) <sup>u</sup>	0.135	1.451	0.250	197.8	15.1	—	20.3	—
1-amino-1,2,4-triazole ( <i>s</i> ) <sup>v</sup>	0.100	1.145	0.246	234.4	13.4	—	18.4	—
4-amino-1,2,4-triazole ( <i>s</i> ) (584-13-4)	0.100	1.148	0.250	435.3	17.2	—	25.7	—
1-nitroxymethyl-1,2,4-triazole	0.148	1.614	0.206	172.3	14.9	—	19.7	—
4-nitroxymethyl-1,2,4-triazole	0.148	1.615	0.250	310.9	18.7	—	27.1	—
<b>Tetrazoles</b>								
1H-tetrazole ( <i>s</i> ) (288-94-8)	0.078	0.933	0.199	390.1	13.2	—	19.7	20.2 <sup>w</sup>
2H-tetrazole (100043-29-6)	0.078	0.931	0.189	333.6	12.0	—	17.4	—
1-methyltetrazole ( <i>s</i> ) (16681-77-9)	0.102	1.163	0.239	204.4	12.8	—	17.0	21.1 <sup>x</sup>
2-methyltetrazole ( <i>l</i> ) (16681-78-0)	0.102	1.161	0.220	152.0	11.2	11.2 <sup>x</sup>	13.9	—
1,5-dimethyltetrazole ( <i>s</i> ) <sup>k</sup> (5144-11-6)	0.125	1.364	0.205	188.6	13.4	20.8 <sup>x</sup>	17.2	—
1-amino-5-methyltetrazole ( <i>s</i> ) <sup>k</sup>	0.118	1.310	0.250	282.1	15.9	—	22.2	—
2-amino-5-methyltetrazole ( <i>l</i> ) <sup>v</sup>	0.118	1.325	0.233	261.2	15.2	—	20.8	—
1-nitroxymethyltetrazole	0.143	1.574	0.218	276.3	17.0	—	23.8	—
2-nitroxymethyltetrazole	0.143	1.572	0.211	140.0	13.9	—	17.8	—

<sup>a</sup>If known, the state of the compound at 298 K and 1 atm is provided. <sup>b</sup>Present work. <sup>c</sup>Majer and Svoboda, 1985. <sup>d</sup>Measured value for 293–309 K (Jimenez et al., 1987). <sup>e</sup>The hydroxy-functionalized analog (CAS no. 3724-26-3) has been synthesized and is a liquid (Jones, 1949). <sup>f</sup>The hydroxy-functionalized analog (CAS no. 822-55-9) has been synthesized. <sup>g</sup>Average of estimates calculated for imidazole and mono- and di-methyl-substituted imidazoles (Gutowski et al., 2005). <sup>h</sup>The hydroxy-functionalized analog (CAS no. 17334-08-6) has been synthesized and is a solid (Jocelyn, 1957). <sup>i</sup>The hydroxy-functionalized analog (CAS no. 38993-84-9) has been synthesized and is a solid (Martin et al., 1968). <sup>j</sup>Martin et al., 1968. <sup>k</sup>Xue et al., 2005. <sup>l</sup>The hydroxy-functionalized analog (CAS no. 936-05-0) has been synthesized (Rufer et al., 1971). <sup>m</sup>Measured value for 268–287 K (Jimenez et al., 1987). <sup>n</sup>Katritzky et al., 2007. <sup>o</sup>The hydroxy-functionalized analog has been synthesized and is a solid (Llamas-Saiz et al., 1992). <sup>p</sup>The hydroxy-functionalized analog (CAS no. 84440-19-7) has been synthesized and is a solid (Banert, 1989). <sup>q</sup>The hydroxy-functionalized analog (CAS no. 78910-04-0) has been synthesized and is a solid (Machin et al., 1984). <sup>r</sup>Jimenez et al., 1989. <sup>s</sup>The hydroxy-functionalized analog (CAS no. 22250-36-8) has been synthesized and is a solid (Norikov et al., 1969). <sup>t</sup>ChemSpider Web site, 2010. <sup>u</sup>Sukhanov et al., 2005. <sup>v</sup>Xue et al., 2004. <sup>w</sup>Kabo et al., 1993. <sup>x</sup>Kozyro et al., 1990. <sup>y</sup>Measured value for 402–473 K (Cundall et al., 1978). <sup>z</sup>Schmidt, 2001.

Table 2. Properties associated with the 0.001 electron/bohr<sup>3</sup> surface of (neutral) P/MCAs, estimates for  $\Delta H_v$  and  $\Delta H_s$ , and comparisons to alternately derived values (continued).<sup>a</sup>

	$V$ nm <sup>3</sup>	$SA$ nm <sup>2</sup>	$\nu$	$\sigma^2$	$\Delta H_v$		$\Delta H_s$	
					b	Other	b	Other
<b>Tetrazoles</b>								
1-methyl-5-nitroxymethyltetrazole	0.165	1.754	0.250	202.4	17.4	—	24.6	—
5-nitroxymethyl-1H-tetrazole	0.142	1.559	0.219	298.1	17.3	—	24.4	—
<b>Guanidines and Hydrazine</b>								
guanidine ( <i>s</i> ) (113-00-8)	0.081	0.980	0.240	252.3	12.2	—	17.4	—
1-nitroguanidine ( <i>s</i> ) (556-88-7)	0.109	1.241	0.232	441.3	17.6	—	25.9	34.1 <sup>y</sup>
nitroxymethylguanidine	0.144	1.565	0.200	246.1	16.0	—	21.7	—
hydrazine ( <i>l</i> ) (302-01-2)	0.051	0.696	0.192	189.9	7.1	10.7 <sup>z</sup>	10.9	—

<sup>a</sup>If known, the state of the compound at 298 K and 1 atm is provided. <sup>b</sup>Present work. <sup>c</sup>Majer and Svoboda, 1985. <sup>d</sup>Measured value for 293–309 K (Jimenez et al., 1987). <sup>e</sup>The hydroxy-functionalized analog (CAS no. 3724-26-3) has been synthesized and is a liquid (Jones, 1949). <sup>f</sup>The hydroxy-functionalized analog (CAS no. 822-55-9) has been synthesized. <sup>g</sup>Average of estimates calculated for imidazole and mono- and di-methyl-substituted imidazoles (Gutowski et al., 2005). <sup>h</sup>The hydroxy-functionalized analog (CAS no. 17334-08-6) has been synthesized and is a solid (Jocelyn, 1957). <sup>i</sup>The hydroxy-functionalized analog (CAS no. 38993-84-9) has been synthesized and is a solid (Martin et al., 1968). <sup>j</sup>Martin et al., 1968. <sup>k</sup>Xue et al., 2005. <sup>l</sup>The hydroxy-functionalized analog (CAS no. 936-05-0) has been synthesized (Rufer et al., 1971). <sup>m</sup>Measured value for 268–287 K (Jimenez et al., 1987). <sup>n</sup>Katritzky et al., 2007. <sup>o</sup>The hydroxy-functionalized analog has been synthesized and is a solid (Llamas-Saiz et al., 1992). <sup>p</sup>The hydroxy-functionalized analog (CAS no. 84440-19-7) has been synthesized and is a solid (Banert, 1989). <sup>q</sup>The hydroxy-functionalized analog (CAS no. 78910-04-0) has been synthesized and is a solid (Machin et al., 1984). <sup>r</sup>Jimenez et al., 1989. <sup>s</sup>The hydroxy-functionalized analog (CAS no. 22250-36-8) has been synthesized and is a solid (Norikov et al., 1969). <sup>t</sup>ChemSpider Web site, 2010. <sup>u</sup>Sukhanov et al., 2005. <sup>v</sup>Xue et al., 2004. <sup>w</sup>Kabo et al., 1993. <sup>x</sup>Kozyro et al., 1990. <sup>y</sup>Measured value for 402–473 K (Cundall et al., 1978). <sup>z</sup>Schmidt, 2001.

### 3.2 Gas-Phase Proton and Methyl Cation Affinities of $\text{NO}_3^-$

$\Delta H_1$  values for  $\text{HNO}_3$  and  $\text{CH}_3\text{NO}_3$  have been derived from measured data. They are 324.5 kcal/mol (Davidson et al., 1977) and 215.7 kcal/mol (Ray and Ogg, 1959; Traeger and McLoughlin, 1981), respectively. In isolation, the difference (109 kcal/mol) would yield  $\Delta G_r(298)$  values for a B-H cycle involving  $\text{HNO}_3$  that is more positive/less negative than an otherwise analogous B-H cycle that involves  $\text{CH}_3\text{NO}_3$  instead. However, as shown in the next section, this consequence is counterbalanced (to varying degrees) by differences in the magnitude of the  $\Delta H_2$  of the P/MCAs.

### 3.3 Gas-Phase Proton and Methyl Cation Affinities for P/MCA

Table 3 shows  $\Delta H_2$  values derived from B3LYP/6-31+G(d,p) results. The table also presents  $\Delta H_2$  values derived from measured data that were found in the open literature. Estimates are within 4 kcal/mol of their corresponding measured value.

For the primary amines and imidazoles, the computational results predict that the substitution of a 2-nitroxyethyl group for an (N-atom bonded) H-atom produces a molecule with a larger  $\Delta H_2$  value. See, for example, the results for ammonia (**6a**), 2-nitroxyethanamine (**10a**), 2-nitroxy-N-(2-nitroxyethyl)ethanamine (**11a**), and 2-nitroxy-N,N-bis(2-nitroxyethyl)ethanamine (**12a**). The results also corroborate Hiskey et al.'s (1991a) speculation that modifying 2-nitroxy-1,1-bis(nitroxymethyl)ethanamine (**15a**) by replacing a nitroxy group with an H-atom [yielding 2-nitroxy-1-nitroxymethyl-1-methylethanamine (**16a**)] or adding a methylene "spacer" [yielding 3-nitroxy-2,2-bis(nitroxymethyl)-propanamine (**17a**)] increases the basicity of the amine group. The latter effect is also observed by comparing the results for 2-nitroxyethanamine (**10a**) and nitroxymethanamine (**13a**).

The results for methyl cation affinities of tertiary amines present a somewhat different story. That is, the successive substitution of 2-nitroxyethyl groups for  $\text{CH}_3$  groups (or the successive substitution of nitroxymethyl groups for H-atoms of methyl groups) leads to successively lower  $\Delta H_2$  values. See, for example, the results for 2-nitroxy-N,N-dimethylethanamine (**1a**), 2-nitroxy-N-(2-nitroxyethyl)-N-methylethanamine (**2a**), and 2-nitroxy-N,N-bis(2-nitroxyethyl)-ethanamine (**3a**). The results for 2,3-dinitroxy-N-(2-nitroxyethyl)-N-methylpropanamine (**5a**) and 2-nitroxy-N-(2-nitroxyethyl)-N-methylethanamine (**2a**) indicate the substitution of 2,3-dinitroxy-propyl group for a 2-nitroxyethyl group is also basicity reducing, while the results for 2-nitroxy-N,N-dimethylethanamine (**1a**) and nitroxy-N,N-dimethylmethanamine (**19a**) indicate that that is also the case for the substitution of a nitroxymethyl group for a 2-nitroxyethyl group. Similar results are observed for analogous substitutions on heterocycles.

The impact of the substitution of methyl, nitro, or amino groups for H-atoms bonded to C-atoms in heterocyclic rings was also investigated. As expected, the  $\Delta H_2$  value of a ring went up (about 3 kcal/mol) when a methyl or amino group was substituted for an H-atom and went down (18–20 kcal/mol) when a nitro group was substituted. The results are consistent with the changes in formation potential observed for such substitutions.

Table 3. Gas-phase proton and methyl cation affinities [ $\Delta H_2$  in kcal/mol] of P/MCAs.

P/MCA	$H^+$		$CH_3^+$	
	a	Other	a	Other
2-nitroxy-N,N-dimethylethanamine (1a)	—	—	115.3	—
2-nitroxy-N-(2-nitroxyethyl)-N-methylethanamine (2a)	—	—	109.8	—
2-nitroxy-N,N-bis(2-nitroxyethyl)ethanamine (3a)	—	—	101.5	—
1-(2-nitroxyethyl)-2-methyl-5-nitroimidazole (4a)	—	—	113.4	—
2,3-dinitroxy-N-(2-nitroxyethyl)-N-methylpropanamine (5a)	—	—	102.2	—
<b>Amines</b>				
ammonia (6a)	204.7	204.0 <sup>c</sup>	104.2	105.3
Methanamine (7a)	215.4	214.9 <sup>c</sup>	—	—
N-methylmethanamine (8a)	222.2	222.2 <sup>c</sup>	—	—
N,N-dimethylmethanamine (9a/18a)	226.3	226.8 <sup>c</sup>	122.7	—
2-nitroxyethanamine (10a)	210.1	—	—	—
2-nitroxy-N-(2-nitroxyethyl)ethanamine (11a)	214.2	—	—	—
2-nitroxy-N,N-bis(2-nitroxyethyl)ethanamine (12a)	216.0	—	—	—
nitroxymethanamine (13a)	197.4	—	—	—
2-amino-2-(hydroxymethyl)-1,3-propanediol (14a)	228.6	—	—	—
2-nitroxy-1,1-bis(nitroxymethyl)ethanamine (15a)	200.9	—	—	—
2-nitroxy-1-nitroxymethyl-1-methylethanamine (16a)	210.1	—	—	—
3-nitroxy-2,2-bis(nitroxymethyl)propanamine (17a)	210.1	—	—	—
nitroxy-N,N-dimethylmethanamine (19a)	—	—	107.4	—
<b>Imidazoles</b>				
1H-imidazole (20a/23a)	226.5	226.8 <sup>b</sup> 225.3 <sup>c</sup>	125.7	—
2-nitroxymethylimidazole (21a)	220.9	—	—	—
5-nitroxymethylimidazole (22a)	219.4	—	—	—
1-methylimidazole (23b/24a)	231.4	231.8 <sup>b</sup> 229.3 <sup>c</sup>	129.9	131.0 <sup>b</sup>
1-nitroxymethylimidazole (25a)	—	—	120.5	—
1-methyl-2-nitroxymethylimidazole (26a)	—	—	121.9	—
1-methyl-5-nitroxymethylimidazole (27a)	—	—	122.3	—
1,5-dimethylimidazole (28a)	—	—	133.6	—
1-methyl-5-aminoimidazole (29a)	—	—	134.6	—
1-methyl-5-nitroimidazole (30a)	—	—	112.4	—
1,2-dimethyl-5-nitroimidazole (31a)	—	—	115.4	—
1-methyl-2-nitroxymethyl-5-nitroimidazole (32a)	—	—	106.3	—
1-ethylimidazole (33a)	—	—	131.4	—
1-(2-nitroxyethyl)imidazole (34a)	—	—	127.8	—
1-(2-nitroxyethyl)-2-methylimidazole (35a)	—	—	130.6	—
1-(2-nitroxyethyl)-4-methylimidazole (36a)	—	—	130.5	—
1-(2-nitroxyethyl)-5-methylimidazole (37a)	—	—	131.3	—

<sup>a</sup>Present work. <sup>b</sup>Gutowski et al., 2005. <sup>c</sup>Hunter and Lias, 1998.

Table 3. Gas-phase proton and methyl cation affinities [ $\Delta H_2$  in kcal/mol] of P/MCAs (continued).

P/MCA	$H^+$		$CH_3^+$	
	a	Other	a	Other
<b>Imidazoles</b>				
1-(2-nitroxyethyl)-2-nitroimidazole (38a)	—	—	107.8	—
1-(2-nitroxyethyl)-4-nitroimidazole (39a)	—	—	110.0	—
1-(2-nitroxyethyl)-5-nitroimidazole (40a)	—	—	110.6	—
<b>Pyrazoles</b>				
1H-pyrazole (41a/44a)	214.7	213.7 <sup>c</sup>	115.8	—
4-nitro-1H-pyrazole (42a)	196.2	—	—	—
3,5-bis(nitroxymethyl)-1H-pyrazole (43a)	209.2	—	—	—
1-methylpyrazole (45a)	220.0	218.0 <sup>c</sup>	119.2	—
1-(nitroxymethyl)pyrazole (46a)	—	—	110.7	—
1-nitroxymethyl-3-methylpyrazole (47a)	—	—	113.8	—
1-nitroxymethyl-4-methylpyrazole (48a)	—	—	113.6	—
1-nitroxymethyl-5-methylpyrazole (49a)	—	—	114.8	—
1-nitroxymethyl-3-nitropyrazole (50a)	—	—	92.7	—
1-nitroxymethyl-4-nitropyrazole (51a)	—	—	95.8	—
1-nitroxymethyl-5-nitropyrazole (52a)	—	—	95.6	—
<b>1,2,3-Triazoles</b>				
1H-1,2,3-triazole (53a/55a/56a) (to 3-position)	214.1	210.2 <sup>c</sup>	117.0	—
1H-1,2,3-triazole (53a/55a/56a) (to 2-position)	—	—	106.6	—
5-nitroxymethyl-1H-1,2,3-triazole (54a) (to 3-position)	200.9	—	—	—
1-methyl-1,2,3-triazole (57a/58a) (to 2-position)	—	—	111.3	—
1-methyl-1,2,3-triazole (57a/58a) (to 3-position)	—	—	122.3	—
1-amino-1,2,3-triazole (59a) (to 3-position)	—	—	120.2	—
1-methyl-5-nitro-1,2,3-triazole (60a) (to 3-position)	—	—	106.7	—
1-nitroxymethyl-1,2,3-triazole (61a/62a) (to 2-position)	—	—	105.9	—
1-nitroxymethyl-1,2,3-triazole (61a/62a) (to 3-position)	—	—	113.2	—
2-nitroxymethyl-1,2,3-triazole (63a/64a)	199.9	—	100.8	—
<b>1,2,4-Triazoles</b>				
1H-1,2,4-triazole (65a/67a) (to 2-position)	—	—	104.3	—
1H-1,2,4-triazole (65a/67a) (to 4-position)	212.2	211.8 <sup>c</sup>	112.4	—
3,5-bis(nitroxymethyl)-1H-1,2,4-triazole (to 4-position)	206.7	—	—	—
4H-1,2,4-triazole (68a)	—	—	121.2	—
1-methyl-1,2,4-triazole (69a) (to 2-position)	—	—	108.6	—
1-methyl-1,2,4-triazole (69a) (to 4-position)	—	—	117.7	—
4-methyl-1,2,4-triazole (70a)	—	—	126.2	—
4-methyl-3-nitro-1,2,4-triazole (71a)	—	—	110.5	—
1-amino-1,2,4-triazole (72a/74a) (to 4-position)	215.6	—	115.3	—
4-amino-1,2,4-triazole (73a/75a) (to 1-position)	221.9	—	124.2	—

<sup>a</sup>Present work. <sup>b</sup>Gutowski et al., 2005. <sup>c</sup>Hunter and Lias, 1998.

Table 3. Gas-phase proton and methyl cation affinities [ $\Delta H_2$  in kcal/mol] of P/MCAs (continued).

P/MCA	$H^+$		$CH_3^+$	
	a	Other	a	Other
<b>1,2,4-Triazoles</b>				
1-nitroxymethyl-1,2,4-triazole (76a/774a) (to 2-position)	—	—	103.6	—
1-nitroxymethyl-1,2,4-triazole (76a/77a) (to 4-position)	—	—	112.2	—
4-nitroxymethyl-1,2,4-triazole (78a)	—	—	117.6	—
<b>Tetrazoles</b>				
1H-tetrazole (79a/80a/81a/82a) (to 2-position)	—	—	91.8	—
1H-tetrazole (79a/80a/81a/82a) (to 3-position)	200.8	—	107.5	—
1H-tetrazole (79a/80a/81a/82a) (to 4-position)	201.2	—	105.4	—
2H-tetrazole (83a/84a/85a) (to 1-position)	—	—	87.1	—
2H-tetrazole (83a/84a/85a) (to 4-position)	—	—	102.8	—
2H-tetrazole (83a/84a/85a) (to 3-position)	—	—	90.9	—
1-methyltetrazole (86a/87a/88a) (to 2-position)	—	—	97.8	—
1-methyltetrazole (86a/87a/88a) (to 3-position)	—	—	113.8	—
1-methyltetrazole (86a/87a/88a) (to 4-position)	—	—	111.6	—
2-methyltetrazole (89a) (to 3-position)	—	—	97.4	—
1,5-dimethyltetrazole (90a) (to 3-position)	—	—	118.9	—
1-amino-5-methyltetrazole (91a) (to 5-position)	—	—	115.7	—
2-amino-5-methyltetrazole (92a) (to 4-position)	—	—	114.4	—
1-nitroxymethyltetrazole (93a/94a/95a) (to 2-position)	—	—	93.7	—
1-nitroxymethyltetrazole (93a/94a/95a) (to 3-position)	—	—	105.4	—
1-nitroxymethyltetrazole (93a/94a/95a) (to 4-position)	—	—	107.4	—
2-nitroxymethyltetrazole (96a/97a/98a) (to 1-position)	—	—	90.0	—
2-nitroxymethyltetrazole (96a/97a/98a) (to 3-position)	—	—	104.5	—
2-nitroxymethyltetrazole (96a/97a/98a) (to 4-position)	—	—	93.6	—
1-methyl-5-nitroxymethyltetrazole (99a)	—	—	110.9	—
5-nitroxymethyl-1H-tetrazole (100a)	200.8	—	—	—
<b>Guanidines and Hydrazine</b>				
guanidine (101a)	238.1	235.7 <sup>c</sup>	—	—
1-nitroguanidine (102a)	209.4	—	—	—
nitroxymethylguanidine (103a)	231.5	—	—	—
hydrazine (104a)	206.2	203.9 <sup>c</sup>	—	—

<sup>a</sup> Present work. <sup>b</sup> Gutowski et al., 2005. <sup>c</sup> Hunter and Lias, 1998.

### 3.4 Lattice Enthalpies

Table 4 shows the cation volumes ( $V^+$ ) that were derived from B3LYP/6-31G(d,p) results, and the  $\Delta H_L$  that were estimated for their nitrate salts. The volumes determined for 1-methyl-3H-imidazolium (**23**) and 1,3-dimethylimidazolium (**24**) are in good agreement with those calculated by Gutowski et al. (2005), and the volumes for 1-methyl-4H-tetrazolium (**82**) nitrate, 1,4-dimethyltetrazolium (**88**) nitrate, and 1,3,5-trimethyltetrazolium (**90**) nitrate are in good agreement with those calculated by Zhang et al. (2010).

The substitution of a nitroxymethyl group for an H-atom produces a cation with a volume that is  $\sim 0.065 \text{ nm}^3$  larger. (See, for example, **6** vs. **13**, **23** vs. **25**, **24** vs. **34**, and **67** vs. **77**.) This, in turn, leads to  $\Delta H_L$  predictions for nitrate salts of the latter that are  $>5 \text{ kcal/mol}$  smaller. Since a reduction in  $\Delta H_L$  leads to a reduction in formation potential, the substitution of a nitroxymethyl group for an H-atom is significantly destabilizing. Similarly, the substitution of a nitroxy group for an H-atom produces a cation with a volume that is  $\sim 0.040 \text{ nm}^3$  larger, and the  $\Delta H_L$  values of the latter's nitrate salts are 4–8 kcal/mol smaller. (See, for example, **15** vs. **16** and **20** vs. **21** or **22**.) The substitution of a nitro group for an H-atom produces cations with volumes that are  $\sim 0.028 \text{ nm}^3$  larger. (See, for example, **24** vs. **30**, and **34** vs. **38**, **39**, and **40**.) In these cases, the  $\Delta H_L$  values of nitrate salts of the latter are 2-3 kcal/mol smaller. Finally, the substitution of a methyl group for an H-atom yields a cation with a volume that is  $\sim 0.024 \text{ nm}^3$  larger. (See, for example, **6** vs. **7**, **7** vs. **8**, **8** vs. **9**, **20** vs. **23**, and **41** vs. **44**.) In these cases, the lattice enthalpies are 4–5 kcal/mol smaller.

Table 4. Cation volumes, lattice enthalpy estimates, and density estimates for nitrate salts.

Cations	$V^+$ $\text{nm}^3$	$\Delta H_L$ $\text{kcal/mol}$	$\rho$ est. <sup>a</sup>	$\rho$ meas.
<b>Cations Synthesized by Drake and Coworkers</b>				
2-nitroxy-N,N,N-trimethylethanam+ (1)	0.186	140	1.40	1.40 <sup>b</sup>
2-nitroxy-N-(2-nitroxyethyl)-N,N-dimethylethanam+ (2)	0.248	135	1.52	1.49 <sup>b</sup>
2-nitroxy-N,N-bis(2-nitroxyethyl)-N-methylethanam+ (3)	0.310	132	1.60	1.63 <sup>b</sup>
1-(2-nitroxyethyl)-2,3-dimethyl-5-nitroim+ (4)	0.246	135	1.57	1.65 <sup>b</sup>
2,3-dinitroxy-N-(2-nitroxyethyl)-N,N-dimethylpropanam+(5)	0.313	131	1.59	1.53 <sup>b</sup>

<sup>a</sup>Present work. <sup>b</sup>Drake et al., 2009. <sup>c</sup>Wagman et al., 1982. <sup>d</sup>Choi et al., 1972. <sup>e</sup>From x-ray crystallographic data (Mylrajan et al., 1985). <sup>f</sup>From x-ray crystallographic data obtained at 173 K (Vitze et al., 2007). <sup>g</sup>From x-ray crystallographic data obtained at 300 K (Mylrajan and Srinivasan, 1988). <sup>h</sup>Hiskey et al., 1991. <sup>i</sup>From x-ray crystallographic data at 295 K (Ilyukhin and Petrosyants, 1993). <sup>j</sup>Emel'yanenko et al., 2009. <sup>k</sup>Wilkes and Zaworotko, 1993. <sup>l</sup>Wang et al., 2007. <sup>m</sup>Wilkes and Zaworotko, 1992. <sup>n</sup>Katritzky et al., 2007. <sup>o</sup>Drake et al., 2003. <sup>p</sup>Drake et al., 2007. <sup>q</sup>Xue et al., 2004. <sup>r</sup>Pace and Flippen-Anderson, 1984. <sup>s</sup>James et al., 1970.



Table 4. Cation volumes, lattice enthalpy estimates, and density estimates for nitrate salts (continued).

Cations	$V^+$	$\Delta H_L$	$\rho$	
	nm <sup>3</sup>	kcal/mol	est. <sup>a</sup>	meas.
<b>Nonquaternary Ammonium Cations</b>				
ammonium (6)	0.030	164 (165) <sup>c</sup>	1.41	1.72 <sup>d</sup>
methanam+ (7)	0.054	157 (157) <sup>c</sup>	1.32	1.40 <sup>e</sup>
N-methylmethanam+ (8)	0.078	153 (149) <sup>c</sup>	1.26	1.29 <sup>f</sup>
N,N-dimethylmethanam+ (9)	0.101	149 (142) <sup>c</sup>	1.23	1.28 <sup>g</sup>
2-nitroxyethanam+ (10)	0.118	147	1.54	—
2-nitroxy-N-(2-nitroxyethyl)ethanam+ (11)	0.206	138	1.59	—
2-nitroxy-N,N-bis(2-nitroxyethyl)ethanam+ (12)	0.290	133	1.63	—
nitroxymethanam+ (13)	0.096	150	1.61	—
Trizma [H <sub>3</sub> NC(CH <sub>2</sub> OH) <sub>3</sub> <sup>+</sup> ] (14)	0.149	151	1.43	—
2-nitroxy-1,1-bis(nitroxymethyl)ethanam+ (15)	0.244	140	1.72	1.69 <sup>h</sup>
2-nitroxy-1-nitroxymethyl-1-methylethanam+ (16)	0.203	144	1.61	1.59 <sup>h</sup>
3-nitroxy-2,2-bis(nitroxymethyl)propanam+ (17)	0.265	138	1.62	1.64 <sup>h</sup>
<b>Quaternary Ammonium Cations</b>				
N,N,N-trimethylmethanam+ (18) (1941-24-8)	0.124	146	1.20	1.24 <sup>i</sup>
nitroxy-N,N,N-trimethylmethanam+ (19)	0.164	142	1.44	—
<b>Imidazolium Cations</b>				
1,3H-imidazolium (20)	0.086	151	1.46	—
2-nitroxymethyl-1,3H-im+ (21)	0.150	143	1.60	—
4-nitroxymethyl-1,3H-im+ (22)	0.150	143	1.60	—
1-methyl-3H-im+ (23)	0.109	148	1.39	1.25 <sup>j</sup> 1.47 <sup>k</sup>
1,3-dimethylim+ (24)	0.133	145	1.34	1.36 <sup>l</sup>
1-nitroxymethyl-3-methylim+ (25)	0.174	141	1.53	—
1,3-dimethyl-2-nitroxymethylim+ (26)	0.196	139	1.49	—
1,3-dimethyl-4-nitroxymethylim+ (27)	0.197	139	1.49	—
1,3,4-trimethylim+ (28)	0.156	142	1.31	—
1,3-dimethyl-4-aminoim+ (29)	0.149	143	1.36	—
1,3-dimethyl-4-nitroim+ (30)	0.162	142	1.50	—
1,2,3-trimethyl-5-nitroim+ (31)	0.183	140	1.46	—

<sup>a</sup> Present work. <sup>b</sup> Drake et al., 2009. <sup>c</sup> Wagman et al., 1982. <sup>d</sup> Choi et al., 1972. <sup>e</sup> From x-ray crystallographic data (Mylrajan et al., 1985). <sup>f</sup> From x-ray crystallographic data obtained at 173 K (Vitze et al., 2007). <sup>g</sup> From x-ray crystallographic data obtained at 300 K (Mylrajan and Srinivasan, 1988). <sup>h</sup> Hiskey et al., 1991. <sup>i</sup> From x-ray crystallographic data at 295 K (Ilyukhin and Petrosyants, 1993). <sup>j</sup> Emel'yanenko et al., 2009. <sup>k</sup> Wilkes and Zaworotko, 1993. <sup>l</sup> Wang et al., 2007. <sup>m</sup> Wilkes and Zaworotko, 1992. <sup>n</sup> Katritzky et al., 2007. <sup>o</sup> Drake et al., 2003. <sup>p</sup> Drake et al., 2007. <sup>q</sup> Xue et al., 2004. <sup>r</sup> Pace and Flippen-Anderson, 1984. <sup>s</sup> James et al., 1970.

Table 4. Cation volumes, lattice enthalpy estimates, and density estimates for nitrate salts (continued).

Cations	$V^+$	$\Delta H_L$	$\rho$	
	nm <sup>3</sup>	kcal/mol	est. <sup>a</sup>	meas.
<b>Imidazolium Cations</b>				
1,3-dimethyl-2-nitroxymethyl-4-nitroim+ (32)	0.224	137	1.61	—
1-ethyl-3-methylim+ (33)	0.157	142	1.30	1.27 <sup>m</sup>
1-(2-nitroxyethyl)-3-methylim+ (34)	0.197	139	1.49	—
1-(2-nitroxyethyl)-2,3-dimethylim+ (35)	0.219	137	1.46	—
1-(2-nitroxyethyl)-3,4-dimethylim+ (36)	0.220	137	1.45	—
1-(2-nitroxyethyl)-3,5-dimethylim+ (37)	0.220	137	1.45	—
1-(2-nitroxyethyl)-3-methyl-2-nitroim+ (38)	0.224	137	1.61	—
1-(2-nitroxyethyl)-3-methyl-4-nitroim+ (39)	0.225	137	1.60	—
1-(2-nitroxyethyl)-3-methyl-5-nitroim+ (40)	0.225	137	1.60	—
<b>Pyrazolium Cations</b>				
1,2H-pyrazolium (41)	0.086	151	1.45	1.59 <sup>n</sup>
4-nitro-1,2H-pyr+ (42)	0.116	147	1.63	—
3,5-bis(nitroxymethyl)-1,2H-pyr+ (43)	0.214	137	1.68	—
1-methylpyr+ (44)	0.110	148	1.39	—
1,2-dimethylpyr+ (45)	0.133	145	1.35	—
1-nitroxymethyl-2-methylpyr+ (46)	0.173	141	1.54	—
1-nitroxymethyl-2,3-dimethylpyr+ (47)	0.195	139	1.50	—
1-nitroxymethyl-2,4-dimethylpyr+ (48)	0.196	139	1.49	—
1-nitroxymethyl-2,5-dimethylpyr+ (49)	0.195	139	1.50	—
1-nitroxymethyl-2-methyl-3-nitropy+ (50)	0.201	138	1.66	—
1-nitroxymethyl-2-methyl-4-nitropy+ (51)	0.203	138	1.65	—
1-nitroxymethyl-2-methyl-5-nitropy+ (52)	0.201	138	1.66	—
<b>1,2,3-Triazolium Cations</b>				
1,3H-1,2,3- triaz+ (53)	0.081	152	1.52	1.57 <sup>o</sup>
4-nitroxymethyl-1,3H-1,2,3triaz+ (54)	0.145	143	1.64	—
1-methyl-3H-1,2,3-triaz+ (55)	0.104	148	1.44	—
2-methyl-1H-1,2,3-triaz+ (56)	0.104	148	1.44	—
1,2-dimethyl-1,2,3-triaz+ (57)	0.127	145	1.39	—
1,3-dimethyl-1,2,3-triaz+ (58)	0.128	145	1.39	—
1-amino-3-methyl-1,2,3-triaz+ (59)	0.121	146	1.44	1.61 <sup>p</sup>
1,3-dimethyl-4-nitro-1,2,3-triaz+ (60)	0.157	142	1.54	—
1-nitroxymethyl-2-methyl-1,2,3-triaz+ (61)	0.168	141	1.58	—
1-nitroxymethyl-3-methyl-1,2,3-triaz+ (62)	0.169	141	1.57	—
1-methyl-2-nitroxymethyl-1,2,3-triaz+ (63)	0.168	141	1.58	—
2-nitroxymethyl-1H-1,2,3-triaz+ (64)	0.146	143	1.64	—

<sup>a</sup>Present work. <sup>b</sup>Drake et al., 2009. <sup>c</sup>Wagman et al., 1982. <sup>d</sup>Choi et al., 1972. <sup>e</sup>From x-ray crystallographic data (Mylrajan et al., 1985). <sup>f</sup>From x-ray crystallographic data obtained at 173 K (Vitze et al., 2007). <sup>g</sup>From x-ray crystallographic data obtained at 300 K (Mylrajan and Srinivasan, 1988). <sup>h</sup>Hiskey et al., 1991. <sup>i</sup>From x-ray crystallographic data at 295 K (Ilyukhin and Petrosyants, 1993). <sup>j</sup>Emel'yanenko et al., 2009. <sup>k</sup>Wilkes and Zaworotko, 1993. <sup>l</sup>Wang et al., 2007. <sup>m</sup>Wilkes and Zaworotko, 1992. <sup>n</sup>Katritzky et al., 2007. <sup>o</sup>Drake et al., 2003. <sup>p</sup>Drake et al., 2007. <sup>q</sup>Xue et al., 2004. <sup>r</sup>Pace and Flippen-Anderson, 1984. <sup>s</sup>James et al., 1970.

Table 4. Cation volumes, lattice enthalpy estimates, and density estimates for nitrate salts (continued).

Cations	$V^+$	$\Delta H_L$	$\rho$	
	nm <sup>3</sup>		est. <sup>a</sup>	meas.
<b>1,2,4-Triazolium Cations</b>				
1,4H-1,2,4- triaz+ (65)	0.080	152	1.52	1.64 <sup>p</sup>
3,5-bis(nitroxymethyl)-1,4H-1,2,4-triaz+ (66)	0.209	138	1.72	—
4-methyl-1H-1,2,4-triaz+ (67)	0.104	149	1.45	—
1-methyl-4H-1,2,4-triaz+ (68)	0.104	149	1.45	—
1,2-dimethyl-1,2,4-triaz+ (69)	0.127	145	1.39	—
1,4-dimethyl-1,2,4-triaz+ (70)	0.128	145	1.39	1.38 <sup>l</sup>
1,4-dimethyl-3-nitro-1,2,4-triaz+ (71)	0.157	142	1.54	—
1-amino-4H-1,2,4-triaz+ (72)	0.097	149	1.52	1.69 <sup>q</sup>
4-amino-1H-1,2,4-triaz+ (73)	0.097	149	1.51	1.60 <sup>o</sup>
1-amino-4-methyl-1,2,4-triaz+ (74)	0.121	146	1.45	1.51 <sup>q</sup>
1-methyl-4-amino-1,2,4-triaz+ (75)	0.121	146	1.45	1.55 <sup>q</sup>
1-nitroxymethyl-2-methyl-1,2,4-triaz+ (76)	0.168	141	1.58	—
1-nitroxymethyl-4-methyl-1,2,4-triaz+ (77)	0.169	141	1.58	—
1-methyl-4-nitroxymethyl-1,2,4-triaz+ (78)	0.169	141	1.58	—
<b>Tetrazolium Cations</b>				
1,4H-tetraz+ (79)	0.076	153	1.58	—
2-methyl-1H-tetraz+ (80)	0.099	149	1.50	—
3-methyl-1H-tetraz+ (81)	0.099	149	1.50	—
1-methyl-4H-tetraz+ (82)	0.099	149	1.50	—
1-methyl-2H-tetraz+ (83)	0.099	149	1.50	—
1-methyl-3H-tetraz+ (84)	0.099	149	1.50	—
2-methyl-3H-tetraz+ (85)	0.099	149	1.50	—
1,2-dimethyltetraz+ (86)	0.122	146	1.44	—
1,3-dimethyltetraz+ (87)	0.122	146	1.44	—
1,4-dimethyltetraz+ (88)	0.123	146	1.43	—
2,3-dimethyltetraz+ (89)	0.122	146	1.44	—
1,3,5-trimethyltetraz+ (90)	0.146	143	1.39	—
1-amino-4,5-dimethyltetraz+ (91)	0.139	144	1.44	1.50 <sup>q</sup>
1,5-dimethyl-3-aminotetraz+ (92)	0.139	144	1.44	1.53 <sup>q</sup>
1-nitroxymethyl-2-methyltetraz+ (93)	0.163	142	1.62	—
1-nitroxymethyl-3-methyltetraz+ (94)	0.164	142	1.62	—
1-nitroxymethyl-4-methyltetraz+ (95)	0.164	142	1.62	—
1-methyl-2-nitroxymethyltetraz+ (96)	0.164	142	1.62	—
1-methyl-3-nitroxymethyltetraz+ (97)	0.164	142	1.62	—
2-nitroxymethyl-3-methyltetraz+ (98)	0.163	142	1.62	—

<sup>a</sup>Present work. <sup>b</sup>Drake et al., 2009. <sup>c</sup>Wagman et al., 1982. <sup>d</sup>Choi et al., 1972. <sup>e</sup>From x-ray crystallographic data (Mylrajan et al., 1985). <sup>f</sup>From x-ray crystallographic data obtained at 173 K (Vitze et al., 2007). <sup>g</sup>From x-ray crystallographic data obtained at 300 K (Mylrajan and Srinivasan, 1988). <sup>h</sup>Hiskey et al., 1991. <sup>i</sup>From x-ray crystallographic data at 295 K (Ilyukhin and Petrosyants, 1993). <sup>j</sup>Emel'yanenko et al., 2009. <sup>k</sup>Wilkes and Zaworotko, 1993. <sup>l</sup>Wang et al., 2007. <sup>m</sup>Wilkes and Zaworotko, 1992. <sup>n</sup>Katritzky et al., 2007. <sup>o</sup>Drake et al., 2003. <sup>p</sup>Drake et al., 2007. <sup>q</sup>Xue et al., 2004. <sup>r</sup>Pace and Flippen-Anderson, 1984. <sup>s</sup>James et al., 1970.

Table 4. Cation volumes, lattice enthalpy estimates, and density estimates for nitrate salts (continued).

Cations	$V^+$	$\Delta H_L$	$\rho$	
	nm <sup>3</sup>	kcal/mol	est. <sup>a</sup>	meas.
<b>Tetrazolium Cations</b>				
1,3-dimethyl-5-nitroxymethyltetraz+ (99)	0.186	140	1.57	—
5-nitroxymethyl-1,3H-tetraz+ (100)	0.140	144	1.70	—
<b>Guanidinium and Hydrazinium Cations</b>				
guanidinium (101) (506-93-4)	0.078	153	1.43	1.44 <sup>f</sup>
1-nitro-1H-guanidinium (102)	0.108	148	1.62	—
nitroxymethylguanidinium (103)	0.141	144	1.59	—
hydrazinium (104)	0.048	159 (171) <sup>c</sup>	1.41	1.66 <sup>s</sup>

<sup>a</sup>Present work. <sup>b</sup>Drake et al., 2009. <sup>c</sup>Wagman et al., 1982. <sup>d</sup>Choi et al., 1972. <sup>e</sup>From x-ray crystallographic data (Mylrajan et al., 1985). <sup>f</sup>From x-ray crystallographic data obtained at 173 K (Vitze et al., 2007). <sup>g</sup>From x-ray crystallographic data obtained at 300 K (Mylrajan and Srinivasan, 1988). <sup>h</sup>Hiskey et al., 1991. <sup>i</sup>From x-ray crystallographic data at 295 K (Ilyukhin and Petrosyants, 1993). <sup>j</sup>Emel'yanenko et al., 2009. <sup>k</sup>Wilkes and Zaworotko, 1993. <sup>l</sup>Wang et al., 2007. <sup>m</sup>Wilkes and Zaworotko, 1992. <sup>n</sup>Katritzky et al., 2007. <sup>o</sup>Drake et al., 2003. <sup>p</sup>Drake et al., 2007. <sup>q</sup>Xue et al., 2004. <sup>r</sup>Pace and Flippen-Anderson, 1984. <sup>s</sup>James et al., 1970.

### 3.5 Density Estimates

Table 4 shows density estimates that were derived from combining calculated  $V^+$  values with a measured value for the molecular volume of  $\text{NO}_3^-$ . Good agreement ( $<0.08$  g/cc difference) between estimates and their corresponding measured value is observed for most salts that do not have an N-H bond. Agreement between estimated and measured values is relatively poor for most salts that have an N-H bond and is worse for salts that have a  $>\text{N-NH}_2$  fragment. The estimates for the nitrate salts of **15**, **16**, and **17**, all of which are relatively large in size, are exceptions.

### 3.6 Gibbs Free Energy Differences

Table 5 shows the  $-T\Delta S$  and  $\Delta G_r(298)$  values computed for all the B-H cycles considered in this study, and it identifies salts whose syntheses have been reported in the open literature. Identified characterizations of salt thermal stabilities are also provided. The subsections that follow discuss relationships between  $\Delta G_r(298)$  values and those characterizations.

Table 5.  $-T\Delta S$ ,  $\Delta G_r(298)$ , and  $\Delta H_f(298)$  predictions (in kcal/mol) for known and notional nitrate salts.

Cation	$-T\Delta S$	$\Delta G_r(298)$	TS	$T_d$	$\Delta H_f(298)$	
	a	a			a	exp
<b>Cations Synthesized by Drake et al.</b>						
2-nitroxy-N,N,N-trimethylethanam+ (1)	4.5	-9	Y <sup>b</sup>	153 <sup>b</sup>	-95	—
2-nitroxy-N-(2-nitroxyethyl)-N,N-dimethylethanam+ (2)	2.4	11	Y <sup>b</sup>	147 <sup>b</sup>	-103	—
2-nitroxy-N,N-bis(2-nitroxyethyl)-N-methylethanam+ (3)	0.4	33	N <sup>b</sup>	145 <sup>b</sup>	-112	—
1-(2-nitroxyethyl)-2,3-dimethyl-5-nitroim+ (4)	2.3	9	N <sup>b</sup>	130 <sup>b</sup>	-65	—
2,3-dinitroxy-N-(2-nitroxyethyl)-N,N-dimethylpropanam+ (5)	0.2	34	N <sup>b</sup>	130 <sup>b</sup>	-111	—
<b>Nonquaternary Ammonium Cations</b>						
ammonium (6)	6.6	-28	Y <sup>c</sup>	>170 <sup>c</sup> 273 <sup>d</sup>	-88	-87 <sup>t</sup>
methanam+ (7)	5.7	-33	—	252 <sup>d</sup> 175 <sup>e</sup>	-87	-85 <sup>t</sup>
N-methylmethanam+ (8)	5.0	-28	—	203 <sup>e</sup>	-89	-84 <sup>t</sup>
N,N-dimethylmethanam+ (9)	4.2	-37	—	186 <sup>e</sup>	-90	-82 <sup>t</sup>
2-nitroxyethanam+ (10)	3.6	-5	N <sup>f</sup>	—	-92	—
2-nitroxy-N-(2-nitroxyethyl)ethanam+ (11)	0.6	8	N <sup>f</sup>	—	-106	—
2-nitroxy-N,N-bis(2-nitroxyethyl)ethanam+ (12)	-2.2	24	N <sup>f</sup>	—	-117	—
nitroxymethanam+ (13)	4.3	5	—	—	-84	—
Trizma [H <sub>3</sub> NC(CH <sub>2</sub> OH) <sub>3</sub> ] <sup>+</sup> (14)	8.2	-15	g	—	-220	—
2-nitroxy-1,1-bis(nitroxymethyl)ethanam+ (15)	4.9	28	—	110 <sup>h</sup>	-117	—
2-nitroxy-1-nitroxymethyl-1methylethanam+ (16)	6.4	9	—	120 <sup>h</sup>	-121	—
3-nitroxy-2,2-bis(nitroxymethyl)propanam+ (17)	4.3	24	—	143 <sup>h</sup>	-126	—

<sup>a</sup>Present work. <sup>b</sup>Drake et al., 2009. <sup>c</sup>Rosser et al., 1963. <sup>d</sup>Jain et al., 1978. <sup>e</sup>Mintz and Jones, 1996. <sup>f</sup>As reported in Urbanski (1965).

<sup>g</sup>Sigma-Aldrich stores this compound at -20 °C (Sigma-Aldrich Web site, 2010). <sup>h</sup>Hiskey et al., 1991. <sup>i</sup>Jain et al., 1978.

<sup>j</sup>Smiglak et al., 2006. <sup>k</sup>Holbrey et al., 2006. <sup>l</sup>Xue et al., 2005. <sup>m</sup>Katritzky et al., 2007. <sup>n</sup>Drake et al., 2003. <sup>o</sup>Drake et al., 2007.

<sup>p</sup>Alkylsulfate and perchlorate salts of this cation have been isolated (Ivashkevich et al., 2009). <sup>q</sup>The perchlorate salt of this cation has been isolated (Sukhanov et al., 2005). <sup>r</sup>Xue et al., 2004. <sup>s</sup>Oxley et al., 2009. <sup>t</sup>Wagman et al., 1982. <sup>u</sup>Matyushin et al., 1985. <sup>v</sup>Wagman, 1964.

<sup>w</sup>Bruenner et al., 1998.

Table 5.  $-T\Delta S$ ,  $\Delta G_r(298)$ , and  $\Delta H_f(298)$  predictions (in kcal/mol) for known and notional nitrate salts (continued).

Cation	$-T\Delta S$	$\Delta G_r(298)$	TS	$T_d$	$\Delta H_f(298)$	
	a	a			a	exp
<b>Quaternary Ammonium Cations</b>						
tetramethylam+ (18)	6.6	-36	—	>300 <sup>i</sup>	-90	—
nitroxy-N,N,N-trimethylmethanam+ (19)	5.2	-5	—	—	-91	—
<b>Imidazolium Cations</b>						
1,3H-imidazolium (20)	4.7	-18	—	—	-55	—
2-nitroxymethyl-1,3H-methylim+ (21)	2.5	-5	—	—	-64	—
4-nitroxymethyl-1,3H-methylim+ (22)	2.5	-3	—	—	-61	—
1-methyl-3H-im+ (23) (B-H XVIIIa)	6.9	-19	Y <sup>j</sup>	156 <sup>k</sup>	-56	—
1-methyl-3H-im+ (23) (B-H XVIIIb)	3.9	-30	Y <sup>j</sup>	156 <sup>k</sup>	—	—
1,3-dimethylim+ (24)	6.1	-31	—	275 <sup>k</sup>	-57	—
1-nitroxymethyl-3-methylim+ (25)	4.7	-8	—	—	-57	—
1,3-dimethyl-2-nitroxymethylim+ (26)	4.0	-8	—	—	-66	—
1,3-dimethyl-4-nitroxymethylim+ (27)	4.0	-8	—	—	-66	—
1,3,4-trimethylim+ (28)	5.3	-32	—	—	-66	—
1,3-dimethyl-4-aminoim+ (29)	5.6	-27	—	—	-56	—
1,3-dimethyl-4-nitroim+ (30)	5.1	-4	—	174 <sup>l</sup>	-41	—
1,2,3-trimethyl-4-nitroim+ (31)	4.4	-4	—	166 <sup>l</sup>	-51	—
1,3-dimethyl-2-nitroxymethyl-4-nitroim+ (32)	3.0	12	—	—	-50	—
1-ethyl-3-methylim+ (33)	5.3	-30	—	—	-64	—
1-(2-nitroxyethyl)-3-methylim+ (34)	4.0	-10	—	—	-68	—
1-(2-nitroxyethyl)-2,3-dimethylim+ (35)	3.3	-9	—	—	-78	—
1-(2-nitroxyethyl)-3,4-dimethylim+ (36)	3.2	-8	—	—	-77	—
1-(2-nitroxyethyl)-3,5-dimethylim+ (37)	3.2	-11	—	—	-77	—

<sup>a</sup>Present work. <sup>b</sup>Drake et al., 2009. <sup>c</sup>Rosser et al., 1963. <sup>d</sup>Jain et al., 1978. <sup>e</sup>Mintz and Jones, 1996. <sup>f</sup>As reported in Urbanski (1965).

<sup>g</sup>Sigma-Aldrich stores this compound at -20 °C (Sigma-Aldrich Web site, 2010). <sup>h</sup>Hiskey et al., 1991. <sup>i</sup>Jain et al., 1978.

<sup>j</sup>Smigłaka et al., 2006. <sup>k</sup>Holbrey et al., 2006. <sup>l</sup>Xue et al., 2005. <sup>m</sup>Katritzky et al., 2007. <sup>n</sup>Drake et al., 2003. <sup>o</sup>Drake et al., 2007.

<sup>p</sup>Alkylsulfate and perchlorate salts of this cation have been isolated (Ivashkevich et al., 2009). <sup>q</sup>The perchlorate salt of this cation has been isolated (Sukhanov et al., 2005). <sup>r</sup>Xue et al., 2004. <sup>s</sup>Oxley et al., 2009. <sup>t</sup>Wagman et al., 1982. <sup>u</sup>Matyushin et al., 1985. <sup>v</sup>Wagman, 1964.

<sup>w</sup>Bruenner et al., 1998.

Table 5.  $-T\Delta S$ ,  $\Delta G_r(298)$ , and  $\Delta H_f(298)$  predictions (in kcal/mol) for known and notional nitrate salts (continued).

Cation	$-T\Delta S$	$\Delta G_r(298)$	TS	$T_d$	$\Delta H_f(298)$	
	a	a			a	exp
<b>Imidazolium Cations</b>						
1-(2-nitroxyethyl)-3-methyl-2-nitroim+ (38)	3.1	13	—	—	-48	—
1-(2-nitroxyethyl)-3-methyl-4-nitroim+ (39)	3.0	18	—	—	-53	—
1-(2-nitroxyethyl)-3-methyl-5-nitroim+ (40)	3.0	8	—	—	-53	—
<b>Pyrazolium Cations</b>						
1,2H-pyr+ (41)	4.7	-10	—	>147 <sup>m</sup>	-32	—
4-nitro-1,2H-pyr+ (42)	3.6	15	N <sup>m</sup>	—	-13	—
3,5-bis(nitroxymethyl)-1,2H-pyr+ (43)	0.3	17	—	—	-55	—
1-methyl-2H-pyr+ (44)	6.9	-13	—	—	-35	—
1,2-dimethylpyr+ (45)	6.2	-21	—	—	-37	—
1-nitroxymethyl-2-methylpyr+ (46)	4.9	-1	—	—	-39	—
1-nitroxymethyl-2,3-dimethylpyr+ (47)	4.1	0	—	—	-49	—
1-nitroxymethyl-2,4-dimethylpyr+ (48)	4.1	0	—	—	-46	—
1-nitroxymethyl-2,5-dimethylpyr+ (49)	4.1	-3	—	—	-49	—
1-nitroxymethyl-2-methyl-3-nitropyr+ (50)	3.9	27	—	—	-19	—
1-nitroxymethyl-2-methyl-4-nitropyr+ (51)	3.8	21	—	—	-24	—
1-nitroxymethyl-2-methyl-5-nitropyr+ (52)	3.9	16	—	—	-20	—
<b>1,2,3-Triazolium Cations</b>						
1,3H-1,2,3-triaz+ (53)	4.8	-13	—	125 <sup>n</sup>	-9	—
4-nitroxymethyl-1,3H-1,2,3-triaz+ (54)	2.7	17	—	—	-7	—
1-methyl-3H-1,2,3-triaz+ (55)	7.1	-11	—	—	-14	—
2-methyl-1H-1,2,3-triaz+ (56)	7.1	-1	—	—	-3	—
1,2-dimethyl-1,2,3-triaz+ (57)	6.3	-12	—	—	-7	—

<sup>a</sup> Present work. <sup>b</sup> Drake et al., 2009. <sup>c</sup> Rosser et al., 1963. <sup>d</sup> Jain et al., 1978. <sup>e</sup> Mintz and Jones, 1996. <sup>f</sup> As reported in Urbanski (1965).

<sup>g</sup> Sigma-Aldrich stores this compound at -20 °C (Sigma-Aldrich Web site, 2010). <sup>h</sup> Hiskey et al., 1991. <sup>i</sup> Jain et al., 1978.

<sup>j</sup> Smiglaka et al., 2006. <sup>k</sup> Holbrey et al., 2006. <sup>l</sup> Xue et al., 2005. <sup>m</sup> Katritzky et al., 2007. <sup>n</sup> Drake et al., 2003. <sup>o</sup> Drake et al., 2007.

<sup>p</sup> Alkylsulfate and perchlorate salts of this cation have been isolated (Ivashkevich et al., 2009). <sup>q</sup> The perchlorate salt of this cation has been isolated (Sukhanov et al., 2005). <sup>r</sup> Xue et al., 2004. <sup>s</sup> Oxley et al., 2009. <sup>t</sup> Wagman et al., 1982. <sup>u</sup> Matyushin et al., 1985. <sup>v</sup> Wagman, 1964.

<sup>w</sup> Bruenner et al., 1998.

Table 5.  $-T\Delta S$ ,  $\Delta G_r(298)$ , and  $\Delta H_f(298)$  predictions (in kcal/mol) for known and notional nitrate salts (continued).

Cation	$-T\Delta S$	$\Delta G_r(298)$	TS	$T_d$	$\Delta H_f(298)$	
	a	a			a	exp
<b>1,2,3-Triazolium Cations</b>						
1,3-dimethyl-1,2,3-triaz+ (58)	6.3	-23	—	—	-18	—
1-amino-3-methyl-1,2,3-triaz+ (59)	6.5	-10	—	185 <sup>o</sup>	15	—
1,3-dimethyl-4-nitro-1,2,3-triaz (60)	5.3	-2	p	—	2	—
1-nitroxymethyl-2-methyl-1,2,3-triaz+ (61)	5.0	6	—	—	-9	—
1-nitroxymethyl-3-methyl-1,2,3-triaz+ (62)	4.9	-1	—	—	-17	—
1-methyl-2-nitroxymethyl-1,2,3-triaz+ (63)	4.9	5	—	—	-9	—
2-nitroxymethyl-1H-1,2,3-triaz+ (64)	2.6	10	—	—	-5	—
<b>1,2,4-Triazolium Cations</b>						
1,4H-1,2,4-triaz+ (65)	4.8	-7	Y <sup>n</sup>	182 <sup>n</sup>	-27	—
3,5-bis(nitroxymethyl)-1,4H-1,2,4-triaz+ (66)	0.4	19	—	—	-50	—
4-methyl-1H-1,2,4-triaz+ (67)	7.1	-9	—	—	-29	—
1-methyl-4H-1,2,4-triaz+ (68)	7.1	-13	—	—	-32	—
1,2-dimethyl-1,2,4-triaz+ (69)	6.3	-10	—	—	-25	—
1,4-dimethyl-1,2,4-triaz+ (70)	6.3	-22	—	160 <sup>l</sup>	-34	—
1,4-dimethyl-3-nitro-1,2,4-triaz+ (71)	5.3	-1	N <sup>l,q</sup>	—	-12	—
1-amino-4H-1,2,4-triaz+ (72)	4.3	-9	—	149 <sup>r</sup>	-3	8 <sup>r</sup>
4-amino-1H-1,2,4-triaz+ (73)	4.3	-8	Y <sup>n</sup>	180 <sup>n,r</sup>	2	-26 <sup>r</sup>
1-amino-4-methyl-1,2,4-triaz+ (74)	6.5	-11	—	217 <sup>r</sup>	-5	-42 <sup>r</sup>
1-methyl-4-amino-1,2,4-triaz+ (75)	6.5	-12	—	221 <sup>r</sup>	-3	-45 <sup>r</sup>
1-nitroxymethyl-2-methyl-1,2,4-triaz+ (76)	4.9	6	—	—	-27	—
1-nitroxymethyl-4-methyl-1,2,4-triaz+ (77)	4.9	-3	—	—	-36	—

<sup>a</sup> Present work. <sup>b</sup> Drake et al., 2009. <sup>c</sup> Rosser et al., 1963. <sup>d</sup> Jain et al., 1978. <sup>e</sup> Mintz and Jones, 1996. <sup>f</sup> As reported in Urbanski (1965).

<sup>g</sup> Sigma-Aldrich stores this compound at -20 °C (Sigma-Aldrich Web site, 2010). <sup>h</sup> Hiskey et al., 1991. <sup>i</sup> Jain et al., 1978.

<sup>j</sup> Smigłaka et al., 2006. <sup>k</sup> Holbrey et al., 2006. <sup>l</sup> Xue et al., 2005. <sup>m</sup> Katritzky et al., 2007. <sup>n</sup> Drake et al., 2003. <sup>o</sup> Drake et al., 2007.

<sup>p</sup> Alkylsulfate and perchlorate salts of this cation have been isolated (Ivashkevich et al., 2009). <sup>q</sup> The perchlorate salt of this cation has been isolated (Sukhanov et al., 2005). <sup>r</sup> Xue et al., 2004. <sup>s</sup> Oxley et al., 2009. <sup>t</sup> Wagman et al., 1982. <sup>u</sup> Matyushin et al., 1985. <sup>v</sup> Wagman, 1964.

<sup>w</sup> Bruenner et al., 1998.



Table 5.  $-T\Delta S$ ,  $\Delta G_r(298)$ , and  $\Delta H_f(298)$  predictions (in kcal/mol) for known and notional nitrate salts (continued).

Cation	$-T\Delta S$	$\Delta G_r(298)$	TS	$T_d$	$\Delta H_f(298)$	
	a	a			a	exp
<b>1,2,4-Triazolium Cations</b>						
1-methyl-4-nitroxymethyl-1,2,4-triaz+ (78)	4.9	-1	—	—	-33	—
<b>Tetrazolium Cations</b>						
1,4H-tetraz+ (79)	9.3	9	—	—	16	—
2-methyl-1H-tetraz+ (80)	7.2	12	—	—	24	—
3-methyl-1H-tetraz+ (81)	7.3	-4	—	—	8	—
1-methyl-4H-tetraz+ (82)	7.2	-2	—	—	10	—
1-methyl-2H-tetraz+ (83)	7.2	14	—	—	26	—
1-methyl-3H-tetraz+ (84)	7.2	-2	—	—	11	—
2-methyl-3H-tetraz+ (85)	7.2	10	—	—	23	—
1,2-dimethyltetraz+ (86)	6.5	5	—	—	19	—
1,3-dimethyltetraz+ (87)	6.5	-11	—	—	3	—
1,4-dimethyltetraz+ (88)	6.4	-8	—	—	5	—
2,3-dimethyltetraz+ (89)	6.5	0	—	—	15	—
1,3,5-trimethyltetraz+ (90)	5.7	-14	—	193 <sup>l</sup>	-11	—
1-amino-4,5-dimethyltetraz+ (91)	5.9	-6	—	170 <sup>f</sup>	19	31 <sup>r</sup>
1,5-dimethyl-3-aminotetraz+ (92)	5.9	-12	—	173 <sup>f</sup>	20	39 <sup>r</sup>
1-nitroxymethyl-2-methyltetraz+ (93)	5.1	19	—	—	17	—
1-nitroxymethyl-3-methyltetraz+ (94)	5.0	8	—	—	5	—
1-nitroxymethyl-4-methyltetraz+ (95)	5.0	6	—	—	3	—
1-methyl-2-nitroxymethyltetraz+ (96)	5.1	17	—	—	17	—
1-methyl-3-nitroxymethyltetraz+ (97)	5.0	3	—	—	3	—
2-nitroxymethyl-3-methyltetraz+ (98)	5.1	14	—	—	14	—

<sup>a</sup>Present work. <sup>b</sup>Drake et al., 2009. <sup>c</sup>Rosser et al., 1963. <sup>d</sup>Jain et al., 1978. <sup>e</sup>Mintz and Jones, 1996. <sup>f</sup>As reported in Urbanski (1965).

<sup>g</sup>Sigma-Aldrich stores this compound at -20 °C (Sigma-Aldrich Web site, 2010). <sup>h</sup>Hiskey et al., 1991. <sup>i</sup>Jain et al., 1978.

<sup>j</sup>Smigłaka et al., 2006. <sup>k</sup>Holbrey et al., 2006. <sup>l</sup>Xue et al., 2005. <sup>m</sup>Katritzky et al., 2007. <sup>n</sup>Drake et al., 2003. <sup>o</sup>Drake et al., 2007.

<sup>p</sup>Alkylsulfate and perchlorate salts of this cation have been isolated (Ivashkevich et al., 2009). <sup>q</sup>The perchlorate salt of this cation has been isolated (Sukhanov et al., 2005). <sup>r</sup>Xue et al., 2004. <sup>s</sup>Oxley et al., 2009. <sup>t</sup>Wagman et al., 1982. <sup>u</sup>Matyushin et al., 1985. <sup>v</sup>Wagman, 1964.

<sup>w</sup>Bruenner et al., 1998.

Table 5.  $-T\Delta S$ ,  $\Delta G_r(298)$ , and  $\Delta H_f(298)$  predictions (in kcal/mol) for known and notional nitrate salts (continued).

Cation	$-T\Delta S$	$\Delta G_r(298)$	TS	$T_d$	$\Delta H_f(298)$	
	a	a			a	exp
<b>Tetrazolium Cations</b>						
1,3-dimethyl-5-nitroxymethyltetraz+ (99)	4.3	4	—	—	-9	—
5-nitroxymethyl-1,3H-tetraz+ (100)	2.8	16	—	—	5	—
<b>Guanidinium and Hydrazinium Cations</b>						
guanidinium (101)	5.0	-35	—	354 <sup>s</sup>	-94	-92 <sup>u</sup>
nitroguanidinium (102)	3.8	6	—	—	-56	—
nitroxymethylguanidinium (103)	2.8	-17	—	—	-97	—
hydrazinium (104)	5.9	-18	—	142 <sup>w</sup>	-49	-60 <sup>v</sup>

<sup>a</sup>Present work. <sup>b</sup>Drake et al., 2009. <sup>c</sup>Rosser et al., 1963. <sup>d</sup>Jain et al., 1978. <sup>e</sup>Mintz and Jones, 1996. <sup>f</sup>As reported in Urbanski (1965).

<sup>g</sup>Sigma-Aldrich stores this compound at -20 °C (Sigma-Aldrich Web site, 2010). <sup>h</sup>Hiskey et al., 1991. <sup>i</sup>Jain et al., 1978.

<sup>j</sup>Smigłaka et al., 2006. <sup>k</sup>Holbrey et al., 2006. <sup>l</sup>Xue et al., 2005. <sup>m</sup>Katritzky et al., 2007. <sup>n</sup>Drake et al., 2003. <sup>o</sup>Drake et al., 2007.

<sup>p</sup>Alkylsulfate and perchlorate salts of this cation have been isolated (Ivashkevich et al., 2009). <sup>q</sup>The perchlorate salt of this cation has been isolated (Sukhanov et al., 2005). <sup>r</sup>Xue et al., 2004. <sup>s</sup>Oxley et al., 2009. <sup>t</sup>Wagman et al., 1982. <sup>u</sup>Matyushin et al., 1985. <sup>v</sup>Wagman, 1964.

<sup>w</sup>Bruenner et al., 1998.

### 3.6.1 Salts With a Nonquaternary Ammonium Cation

The data acquired for nitrate salts with nonquaternary ammonium cations are generally consistent with the hypothesized correlation between thermal stability and computed  $\Delta G_r(298)$  values. Relatively large negative  $\Delta G_r(298)$  values for the nitrate salts of ammonium (**6**), methan ammonium (**7**), N-methylmethan ammonium (**8**), and N,N-dimethylmethan ammonium (**9**) nitrate were obtained, and all have DSC decomposition onsets  $\gg 150$  °C. The only other salts in the table with a primary, secondary, or tertiary ammonium group and negative  $\Delta G_r(298)$  values are trizma (**14**) nitrate (CAS no. 41521-38-4) and 2-nitroxyethyl ammonium (**7**) nitrate. Trizma nitrate is commercially available from Sigma-Aldrich, so its thermal stability might be presumed. However, the Sigma-Aldrich Web site reports its storage temperature to be  $-20$  °C, suggesting it might not meet the standard for thermal stability recognized in this report. 2-Nitroxyethyl ammonium (**7**) nitrate has been observed to react violently when raised to  $75$  °C. Positive  $\Delta G_r(298)$  values were obtained for 2-nitroxy-N-(2-nitroxyethyl) ethan ammonium (**11**) nitrate and 2-nitroxy-N,N-bis(2-nitroxyethyl) ethan ammonium (**12**) nitrate, and as has been noted, they are unstable at temperatures  $<75$  °C. Similarly, the three compounds in the table that were synthesized and characterized by Hiskey et al. (1991a)—the 2-nitroxy-1,1-bis(nitroxymethyl) ethan ammonium (**15**) nitrate, 2-nitroxy-1-nitroxymethyl-1methylethan ammonium (**16**) nitrate, and 3-nitroxy-2,2-bis(nitroxy-methyl)propan ammonium (**17**) nitrate—all have fairly high positive  $\Delta G_r(298)$  values and DSC decomposition onsets  $<150$  °C. (2-Nitroxy-1,1-bis(nitroxymethyl)ethan ammonium (**15**) nitrate was observed to evolve  $\text{HNO}_3$  after 4 weeks at room temperature.)

### 3.6.2 Salts With a Quaternary Ammonium Cation

The data acquired for nitrate salts with quaternary ammonium cations generally corroborate the hypothesized correlation between thermal stability and computed  $\Delta G_r(298)$  values. A relatively large negative  $\Delta G_r(298)$  value was calculated for tetramethyl ammonium (**18**) nitrate, and a DSC decomposition onset  $\gg 150$  °C has been reported for it. The  $\Delta G_r(298)$  values for the four nitrate salts with quaternary ammonium cations that Drake et al. (2009) synthesized also align with the thermal stabilities observed for them. 2-Nitroxy-N,N,N-trimethylethanamine (**1**) nitrate, whose  $\Delta G_r(298)$  was determined to be  $-9$  kcal/mol, was the only one that did not exhibit significant mass loss after 24 h at  $75$  °C and had a DSC decomposition onset  $\geq 150$  °C.  $\Delta G_r(298)$  values for the other three—namely, 2-nitroxy-N-(2-nitroxyethyl)-N,N-dimethylethan ammonium (**2**), 2-nitroxy-N,N-bis(2-nitroxyethyl)-N-methylethan ammonium (**3**), and 2,3-dinitroxy-N-(2-nitroxyethyl)-N,N-dimethylpropan ammonium (**5**)—are positive, and each was observed to begin decomposing in DSC experiments at a temperature  $<150$  °C.

### 3.6.3 Salts Having a Cation With a Heterocyclic Ring

3.6.3.1 Cations With an Imidazolium Ring. The  $\Delta G_r(298)$  values computed for 1-(2-nitroxyethyl)-2,3-dimethyl-5-nitroimidazolium (**4**) nitrate, which has been observed to be

unstable, and the nitrate salts of 1-methyl-3H-imidazolium (**23**), 1,3-dimethylimidazolium (**24**), 1,3-dimethyl-4-nitroimidazolium (**30**), and 1,2,3-trimethyl-4-nitroimidazolium (**31**) nitrate, all of which have been observed to be stable, indicate the validity of the hypothesized correlation between computed  $\Delta G_r(298)$  values and thermal stability. As such, the negative  $\Delta G_r(298)$  values found for the notional imidazolium nitrates whose cations have a single (primary) nitroxy group suggest they will be stable, while the positive  $\Delta G_r(298)$  values for the nitrate salts of the three notional imidazolium cations with two  $\text{NO}_x$  groups suggest they will be unstable. Corroborating the latter predictions, Katritzky et al. (2006) report that they were unable to N-alkylate or protonate dinitro-substituted imidazoles.

3.6.3.2 Cations With a Pyrazolium Ring. The evidence validating the hypothesized correlation between the thermal stability of pyrazolium nitrates and computed  $\Delta G_r(298)$  values is extremely limited. Katritzky and coworkers synthesized 1,2H-pyrazolium (**41**) nitrate, but they did not report a DSC decomposition onset for it. They report its melting point to be 147 °C but do not report the temperature at which it begins to decompose. Therefore, it does not represent a definitive validating case. 4-Nitro-1,2H-pyrazolium (**42**) nitrate, which was observed to decompose quickly at room temperature, does. As such, the negative  $\Delta G_r(298)$  estimates for the nitrate salts of 1-methyl-2H-pyrazolium (**44**) and 1,2-dimethylpyrazolium (**45**) suggest they will be stable. All  $\Delta G_r(298)$  estimates for pyrazolium salts with even a single nitroxy group are positive, which suggests they will not be stable for 24 h at 75 °C.

Pyrazolium salts are known (in general) to be less stable than imidazolium salts, and the significant difference in  $\Delta G_r(298)$  estimates for constitutional isomers is consistent with that observation. For example, the  $\Delta G_r(298)$  estimate for 1-nitroxymethyl-3-methylimidazolium (**25**) nitrate is  $-8$  kcal/mol, while the  $\Delta G_r(298)$  estimate for 1-nitroxymethyl-2-methylpyrazolium (**46**) nitrate is  $-1$  kcal/mol. The weakly negative  $\Delta G_r(298)$  estimates for nitrate salts having a cation with a pyrazolium ring and a single nitroxymethyl group suggest the prospects for synthesizing a stable nitrate salt with a pyrazolium ring and more than one  $\text{NO}_x$  group are highly unlikely.

3.6.3.3 Cations With a 1,2,3-Triazolium or 1,2,4-Triazolium Ring. The evidence available for validating the hypothesized correlation between the thermal stability of triazolium nitrates and computed  $\Delta G_r(298)$  values is reasonably extensive and tends to support it. Negative  $\Delta G_r(298)$  values were calculated for all triazolium nitrates meeting the thermal stability criteria, and  $\Delta G_r(298)$  values are very weakly negative for two salts whose thermal stabilities are suspect: 1,3-dimethyl-4-nitro-1,2,3-triazolium (**60**) nitrate and 1,4-dimethyl-4-nitro-1,2,4-triazolium (**71**). The positive  $\Delta G_r(298)$  value found for 1,4-dimethyl-3-nitro-1,2,4-triazolium (**71**) nitrate, whose instability can be surmised from the difficulty Xue et al. (2005) had quaternizing 1-methyl-3-nitro-1,2,4-triazole (**71a**), also corroborates the hypothesis. On the other hand, 1-amino-4H-1,2,4-triazolium (**72**) nitrate's  $\Delta G_r(298)$  value would suggest that it is more stable than 4-amino-1H-1,2,4-triazolium (**73**) nitrate and not marginally stable. More disquieting, however, is the negative  $\Delta G_r(298)$  value calculated for the thermally unstable 1,3H-1,2,3-triazolium (**53**) nitrate.

Taken together, the comparisons indicate that the predictive capability of the method is not entirely reliable, but its results are worth considering. They include negative  $\Delta G_r(298)$  values for (notional) salts with triazolium rings and no  $\text{NO}_x$  groups that suggest some will be stable. The weakly negative  $\Delta G_r(298)$  values for the nitrate salts of 1-(nitroxymethyl)-3-methyl-1,2,3-triazolium (**62**), 1-(nitroxymethyl)-4-methyl-1,2,4-triazolium (**77**), and 1-methyl-4-(nitroxymethyl)-1,2,4-triazolium (**78**) are not encouraging. The  $\Delta G_r(298)$  values for cations with a triazolium ring and more than one  $\text{NO}_x$  group suggest that the prospects for their being stable for 24 h at 75 °C are very poor.

3.6.3.4. Cations With a Tetrazolium Ring. The experimental evidence available for validating the hypothesized correlation between the thermal stability of tetrazolium nitrates and computed  $\Delta G_r(298)$  values is fairly limited. Results for 1,3,5-trimethyltetrazolium (**90**) nitrate, 1-amino-4,5-dimethyltetrazolium (**91**) nitrate, and 1,5-dimethyltetrazolium (**92**) nitrate corroborate the hypothesis. In addition, no report of the synthesis of tetrazolium (**79**) nitrate was found in the open literature. The positive  $\Delta G_r(298)$  value found for it may explain that result. As such, there is a measure of confidence in a  $\Delta G_r(298)$  value's ability to predict the thermal stability of tetrazolium nitrates. Some with no  $\text{NO}_x$  groups also have negative  $\Delta G_r(298)$  values and therefore are expected to be stable. But none with a nitroxymethyl group were found to have a negative  $\Delta G_r(298)$  value, which suggests that the prospects for such salts being stable for 24 h at 75 °C are poor.

### 3.6.4 Salts With a Guanidinium or Hydrazinium Group

Although DSC decomposition onsets for a relatively large number of guanidinium nitrates have been published (Gao et al., 2005), a  $\Delta G_r(298)$  value for guanidinium (**101**) nitrate was the only one calculated for comparison. The comparison supports the proposed hypothesis. (The result for hydrazinium (**104**) nitrate does not.) Nitroguanidinium (**102**) nitrate has been isolated and its crystal structure characterized (Pace and Flippen-Anderson, 1984), but a characterization of its thermal stability could not be found. Evidence for the synthesis of N-(2-nitroxyethyl)-N'-nitroguanidinium nitrate has been reported (McKay and Milks, 1950), but it was not isolated. The negative  $\Delta G_r(298)$  value found for the notional nitrate salt of 1-nitroxymethyl-1H-guanidinium (**103**) suggests that it will be stable. Given the large positive increase in  $\Delta G_r(298)$  effected by the substitution of a  $-\text{CH}_2\text{ONO}_2$  group for an H-atom, it is doubtful that salts with more  $-\text{CH}_2\text{ONO}_2$  groups will be predicted to be stable for 24 h at 75 °C.

## 3.7 Heat of Formation Estimates

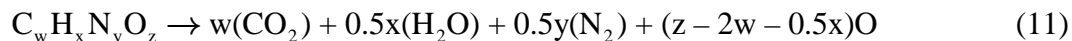
Table 5 lists  $\Delta H_f(298)$  estimates that were obtained for all the nitrate salts considered in this study. Data available for validating the estimates are, however, sparse. Most of the uncertainty in the  $\Delta H_f(298)$  estimates is associated with the  $\Delta H_L$  estimates. Good agreement between measured and estimated  $\Delta H_f(298)$  values is observed for ammonium (**6**) nitrate, methylammonium (**7**) nitrate, dimethylammonium (**8**) nitrate, and trimethylammonium (**9**) nitrate, but these salts were in the set employed by Gutowski et al. (2007) to reparameterize the

Jenkins model. Therefore, good agreement is to be expected. However, the estimates do not predict the trend toward more positive values for the sequence (6 → 7 → 8 → 9) observed in the measured values. The trend is produced if the calculated ion-pair volumes are scaled as done by Gutowski et al. for calculated (not measured) volumes. But as mentioned in section 2, the ion-pair volumes employed in this study combine a calculated cation volume with a measured value for NO<sub>3</sub><sup>-</sup>, and if scaled, the resulting volumes lead to density estimates that are too high and ΔH<sub>L</sub> estimates that are too negative.

Except for guanidium (101) nitrate, all other compounds for whom a measured ΔH<sub>f</sub>(298) was found have an >N-NH<sub>2</sub> fragment, and all ΔH<sub>f</sub>(298) estimates for them are >10 kcal/mol different from their respective measured value. In all of these cases, the ion-pair volumes employed to calculate ΔH<sub>L</sub> yield density estimates that are too low. Thus it could be expected that they would underpredict the magnitude of ΔH<sub>L</sub> and yield ΔH<sub>f</sub>(298) estimates that are too positive. This is true in every case except 1-amino-4H-1,2,4-triazolium (72) nitrate. Given the sparseness of the measured data that was identified in the attempt to validate the model's predictions for ΔH<sub>f</sub>(298) values, particularly the fact that no measured values for nitrate salts with nitroxy-functionalized cations could be identified, the reliability of any model for estimating ΔH<sub>f</sub>(298) values for such compounds is going to be fairly uncertain. The gas-phase ΔH<sub>f</sub>(298) values for the cations are likely to be within ±3 kcal/mol their actual value. Uncertainty in the ΔH<sub>L</sub> estimates is more difficult to quantify. Since the density estimates based on unscaled volumes calculated for the salts with the nitroxy-functionalized cations synthesized by Drake et al. (2009) are in good agreement with measured values, they were considered the best choice for calculating ΔH<sub>L</sub>. ΔH<sub>f</sub>(298) estimates obtained by Drake et al. (2009) using an alternate (group additivity-based) method are more negative by 8–59 kcal/mol.

## 4. Discussion

To be considered an oxidizer, a salt must have a stoichiometry such that the “O-atom balance” ( $z - 2w - 0.5x$ ) for the hypothetical reaction



is a positive number, i.e.,  $z > 2w + 0.5x$ . For ammonium (6) nitrate, (H<sub>4</sub>N<sub>2</sub>O<sub>3</sub>), the O-atom balance is one (+1.0). Since the O-atom balance for a nitroxymethyl (CH<sub>2</sub>NO<sub>3</sub>) group is zero, the substitution of it for an H-atom (whose O-atom balance is -0.5) produces a salt whose net O-atom balance is 0.5 higher. Substitution of a nitroxyethyl (C<sub>2</sub>H<sub>4</sub>NO<sub>3</sub>) group for an H-atom produces a salt whose net oxygen balance is 2.5 lower. Similarly, substitution of a methyl (CH<sub>3</sub>) group for an H-atom produces to a salt whose net O-atom balance is 3.0 lower. Therefore, for every (acidic) H-atom that is replaced with a methyl group in the hope of obtaining a salt with

better thermal stability, a nitroxy group has to be added as well in order to produce a net-neutral change in the O-atom balance. Even the highly substituted N,N,N-tris(nitroxymethyl)-methanamine nitrate (C<sub>4</sub>H<sub>9</sub>N<sub>2</sub>O<sub>12</sub>) has a negative O-atom balance (-0.5).

If it is assumed that there can be no more than one nitroxy group bonded to a C-atom, every C-atom of a quaternary ammonium cation must have a nitroxy group in order for its nitrate salt to have a positive O-atom balance. The  $\Delta G_r(298)$  value for the nitrate salt of (monosubstituted) nitroxy-N,N,N-trimethylmethan ammonium (**19**) suggests that it will be stable. However, because it withdraws electron density from the ammonium group N-atom, the nitroxymethyl group significantly reduces the N-atom's affinity for other chains or H-atoms. The destabilizing influence of that reduction is captured by the 27 kcal/mol more positive  $\Delta G_r(298)$  value of nitroxy-N,N,N-trimethylmethanamine (**1**) nitrate vs. tetramethylammonium (**18**) nitrate's. The expectation of similar differences being produced by the addition of more nitroxy groups does not bode well for the stability of nitrate salts of quaternary ammonium cations with more than one nitroxymethyl chain.

The N-atoms of cations with a heterocyclic ring have only one or two acidic protons instead of the three associated with a primary ammonium group, and C-atoms in such rings are bonded to only one H-atom instead of the two or three that bond to an alkyl group C-atom. Thus cations with a heterocyclic ring would appear to have more potential to be quaternized and have a positive O-atom balance than those with an ammonium group. However, the  $\Delta G_r(298)$  values that were calculated for nitrate salts with heterocyclic cations suggest that the benefits afforded by such platforms are very limited. For example, the  $\Delta G_r(298)$  values for 1,3-dimethyl-2-nitroxymethylimidazolium (**26**) nitrate and 1,3-dimethyl-4-nitroxymethylimidazolium (**27**) nitrate are both 23 kcal/mol more positive than 1,3-dimethylimidazolium (**24**) nitrate.

Another aspect of the study deserving mention is that despite positive  $\Delta G_r(298)$  values being calculated for 2-nitroxy-N-(2-nitroxyethyl)-N,N-dimethylethan ammonium (**2**) nitrate and 2,3-dinitroxy-N-(2-nitroxyethyl)-N,N-dimethylpropan ammonium (**5**) nitrate, these salts showed no noticeable decomposition after being stored for many months at room temperature. This suggests that there are kinetic barriers to their decomposition that are not easily surmounted at room temperature. Thus a study of kinetic barriers to the decomposition of such salts might provide insight into factors that could be exploited to design more thermally stable ones.

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## 5. Summary

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With EQBR and SERDP funding, the potential of nitrate salts with nitroxy-functionalized cations to be oxidizers for solid rocket propellant formulations was investigated. To examine a hypothesis that the thermal stability of an organic nitrate salt would correlate with the Gibbs free energy difference [ $\Delta G_r(298)$ ] between it and expected products of the first step of its

decomposition, computationally based  $\Delta G_r(298)$  estimates were obtained for relevant salts whose responses to thermal loads have been reported. The data acquired generally supports the hypothesis. Considered to be thermally stable if they exhibited <1% mass loss after being held at 75 °C for 24 h, or they did not noticeably decompose in DSC experiments at temperatures below 150 °C, salts for whom negative  $\Delta G_r(298)$  values were calculated usually meet the criteria while those for whom positive  $\Delta G_r(298)$  values were calculated usually do not. Since the computation of  $\Delta G_r(298)$  estimates is relatively quick and low-cost compared to a synthesis effort, it represents a practical means for screening the potential viability of rocket propellant ingredient candidates from this class of compounds.

In addition to establishing the screening method,  $\Delta G_r(298)$  values for a number of notional nitrate salts were obtained.  $\Delta H_f(298)$  and density estimates for these salts were obtained as well. Comparisons of density estimates obtained by two published methods and one developed and employed for the current study indicate that none can be applied with confidence across the entire range of cations considered in this study, and thus that additional study is warranted. The  $\Delta G_r(298)$  results indicate that it is highly unlikely any nitrate salt with cation having more than two NO<sub>x</sub> groups will be thermally stable for 24 h at 75 C. Therefore, stable candidates from the class are unlikely to be oxidizers per se. Nevertheless, to the extent they merit consideration as additives for propellants or explosives, the results of this study offer some guidance for candidate design and selection.



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## 6. References

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## Appendix. Data for Estimating Enthalpy of Formation Values

Table A-1 provides B3LYP/6-31+G(d,p)-determined gas-phase enthalpies at 298 K [ $H_g(298)$ ] and measured/derived gas-phase enthalpies of formation [ $\Delta H_{fg}(298)$ ] for species employed in isodesmic reaction schemes designed to obtain predictions for gas-phase enthalpies of formation [ $\Delta H_{fg}(298)$ ] for modeled cations. B3LYP/6-31+G(d,p)-determined  $H_g(298)$  values for the cations are provided in table A-2.

Table A-1.  $H_g(298)$  estimates derived from B3LYP/6-31+G(d,p) results and gas-phase enthalpy of formation [ $\Delta H_{fg}(298)$ ] values derived from measured data.

	$H_g(298)$ hartrees	$\Delta H_{fg}(298)$ kcal/mol	Ref
CH <sub>4</sub>	-40.477541	-17.8	a
CH <sub>3</sub> CH <sub>3</sub>	-79.762616	-20.0	b
NH <sub>3</sub>	-56.528796	-11.0	a
NH <sub>2</sub> NH <sub>2</sub>	-111.823884	22.8	a
CH <sub>3</sub> NH <sub>2</sub>	-95.803447	-5.6	c,d
(CH <sub>3</sub> ) <sub>2</sub> NH	-135.083592	-4.7	e
(CH <sub>3</sub> ) <sub>2</sub> NNO <sub>2</sub>	-339.577827	-1.2	f
CH <sub>3</sub> NO <sub>2</sub>	-244.973602	-19.3	g
CH <sub>3</sub> ONO <sub>2</sub>	-320.149105	-29.2	h
CH <sub>3</sub> CH <sub>2</sub> ONO <sub>2</sub>	-359.442423	-37.0	i
CH <sub>3</sub> CH <sub>2</sub> OH	-154.972890	-56.1	j,k
H <sup>+</sup>	—	365.7	a
NH <sub>4</sub> <sup>+</sup>	-56.852617	150.7	$\Delta H_{fg}(\text{NH}_3)$ : a; PA(NH <sub>3</sub> ): l
CH <sub>3</sub> NH <sub>3</sub> <sup>+</sup>	-96.144388	146.7	$\Delta H_{fg}(\text{CH}_3\text{NH}_2)$ : c,d; PA(CH <sub>3</sub> NH <sub>2</sub> ): l
(CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> <sup>+</sup>	-135.435317	140.3	$\Delta H_{fg}((\text{CH}_3)_2\text{NH})$ : e; PA((CH <sub>3</sub> ) <sub>2</sub> NH): l
(CH <sub>3</sub> ) <sub>3</sub> NH <sup>+</sup>	-174.724749	134.7	$\Delta H_{fg}((\text{CH}_3)_3\text{N})$ : e; PA((CH <sub>3</sub> ) <sub>3</sub> N): j
(CH <sub>3</sub> ) <sub>4</sub> N <sup>+</sup>	-214.011571	131.2	$\Delta H_{fg}((\text{CH}_3)_3\text{N})$ : e; PA((CH <sub>3</sub> ) <sub>3</sub> N): l; m
1,3H-imidazolium	-226.518133	171.4	$\Delta H_{fg}(\text{imidazole})$ : n,o; PA(imidazole): l
1,2H-pyrazolium	-226.482835	194.4	$\Delta H_{fg}(\text{pyrazole})$ : n,o; PA(pyrazole): l
1,2,3H-triazolium	-242.516491	218.1	$\Delta H_{fg}(\text{1H-123-triaz})$ : p; PA(1H-123-triaz): l
1,4H-1,2,4-triazolium	-242.539728	200.0	$\Delta H_{fg}(\text{1H-124-triaz})$ : q; PA(1H-124-triaz): l
1,4H-tetrazolium	-258.534984	244.3	$\Delta H_{fg}(\text{1H-tetraz})$ : r; PA(1H-tetraz): l
guanidium	-205.69205	134.0	$\Delta H_{fg}(\text{guanidine})$ : s; PA(guanidine): l
hydrazinium	-112.150096	184.6	$\Delta H_{fg}(\text{hydrazine})$ : a; PA(hydrazine): l
NO <sub>3</sub> <sup>-</sup>	-280.362751	-74.8	t

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Table A-2.  $H_g(298)$  estimates derived from B3LYP/6-31+G(d,p) results.

<b>Cations</b>	<b><i>H</i> hartrees</b>
<b>Cations Synthesized by Drake and Coworkers</b>	
2-nitroxy-N,N,N-trimethylethanam+ (1)	-532.965055
2-nitroxy-N-(2-nitroxyethyl)-N,N-dimethylethanam+ (2)	-851.919601
2-nitroxy-N,N-bis(2-nitroxyethyl)-N-methylethanam+ (3)	-1170.873725
1-(2-nitroxyethyl)-2,3-dimethyl-5-nitroim+ (4)	-867.836021
2,3-dinitroxy-N-(2-nitroxyethyl)-N,N-dimethylpropanam+(5)	-1170.871626
<b>Non-quaternary Ammonium Cations</b>	
ammonium (6)	-56.852617
methanam+ (7)	-96.144388
N-methylmethanam+ (8)	-135.435317
N,N-dimethylmethanam+ (9)	-174.724749
2-nitroxyethanam+ (10)	-415.106623
2-nitroxy-N-(2-nitroxyethyl)ethanam+ (11)	-773.357773
2-nitroxy-N,N-bis(2-nitroxyethyl)ethanam+ (12)	-1131.59883
nitroxymethanam+ (13)	-375.808237
Trizma [ $H_3NC(CH_2OH)_3^+$ ] (14)	-439.669519
2-nitroxy-1,1-bis(nitroxymethyl)ethanam+ (15)	-1053.022034
2-nitroxy-1-nitroxymethyl-1-methylethanam+ (16)	-773.363245
3-nitroxy-2,2-bis(nitroxymethyl)propanam+ (17)	-1092.31519
<b>Quaternary Ammonium Cations</b>	
N,N,N-trimethylmethanam+ (18)	-214.011556
nitroxy-N,N,N-trimethylmethanam+ (19)	-493.674002
<b>Imidazolium Cations</b>	
1,3H-imidazolium (20)	-226.518133
2-nitroxymethyl-1,3H-im+ (21)	-545.480036
4-nitroxymethyl-1,3H-im+ (22)	-545.476531
1-methyl-3H-im+ (23)	-265.809298
1,3-dimethylim+ (24)	-305.099434
1-nitroxymethyl-3-methylim+ (25)	-584.759570
1,3-dimethyl-2-nitroxymethylim+ (26)	-624.057269
1,3-dimethyl-4-nitroxymethylim+ (27)	-624.057499
1,3,4-trimethylim+ (28)	-344.398936
1,3-dimethyl-4-aminoim+ (29)	-360.446768
1,3-dimethyl-4-nitroim+ (30)	-509.571884
1,2,3-trimethyl-5-nitroim+ (31)	-548.873762
1,3-dimethyl-2-nitroxymethyl-4-nitroim+ (32)	-828.528747
1-ethyl-3-methylim+ (33)	-344.392119
1-(2-nitroxyethyl)-3-methylim+ (34)	-624.060622
1-(2-nitroxyethyl)-2,3-dimethylim+ (35)	-663.360883

Table A-2.  $H_g(298)$  estimates derived from B3LYP/6-31+G(d,p) results (continued).

<b>Cations</b>	<b><i>H</i> hartrees</b>
<b>Imidazolium Cations</b>	
1-(2-nitroxyethyl)-3,4-dimethylim+ (36)	-663.360095
1-(2-nitroxyethyl)-3,5-dimethylim+ (37)	-663.359268
1-(2-nitroxyethyl)-3-methyl-2-nitroim+ (38)	-828.525127
1-(2-nitroxyethyl)-3-methyl-4-nitroim+ (39)	-828.533329
1-(2-nitroxyethyl)-3-methyl-5-nitroim+ (40)	-828.533598
<b>Pyrazolium Cations</b>	
1,2H-pyrazolium (41)	-226.482835
4-nitro-1,2H-pyr+ (42)	-430.954257
3,5-bis(nitroxymethyl)-1,2H-pyr+ (43)	-864.411449
1-methylpyr+ (44)	-265.777133
1,2-dimethylpyr+ (45)	-305.068499
1-nitroxymethyl-2-methylpyr+ (46)	-584.731362
1-nitroxymethyl-2,3-dimethylpyr+ (47)	-624.031989
1-nitroxymethyl-2,4-dimethylpyr+ (48)	-624.028072
1-nitroxymethyl-2,5-dimethylpyr+ (49)	-624.032526
1-nitroxymethyl-2-methyl-3-nitropyr+ (50)	-789.198102
1-nitroxymethyl-2-methyl-4-nitropyr+ (51)	-789.206008
1-nitroxymethyl-2-methyl-5-nitropyr+ (52)	-789.199296
<b>1,2,3-Triazolium Cations</b>	
1,3H-1,2,3- triaz+ (53)	-242.516491
4-nitroxymethyl-1,3H-1,2,3triaz+ (54)	-561.461558
1-methyl-3H-1,2,3-triaz+ (55)	-281.813648
2-methyl-1H-1,2,3-triaz+ (56)	-281.797068
1,2-dimethyl-1,2,3-triaz+ (57)	-321.091707
1,3-dimethyl-1,2,3-triaz+ (58)	-321.109208
1-amino-3-methyl-1,2,3-triaz+ (59)	-337.121309
1,3-dimethyl-4-nitro-1,2,3-triaz+ (60)	-525.576254
1-nitroxymethyl-2-methyl-1,2,3-triaz+ (61)	-600.755460
1-nitroxymethyl-3-methyl-1,2,3-triaz+ (62)	-600.766961
1-methyl-2-nitroxymethyl-1,2,3-triaz+ (63)	-600.755560
2-nitroxymethyl-1H-1,2,3-triaz+ (64)	-561.461636
<b>1,2,4-Triazolium Cations</b>	
1,4H-1,2,4- triaz+ (65)	-242.539728
3,5-bis(nitroxymethyl)-1,4H-1,2,4-triaz+ (66)	-880.468989
4-methyl-1H-1,2,4-triaz+ (67)	-281.832561
1-methyl-4H-1,2,4-triaz+ (68)	-281.836627
1,2-dimethyl-1,2,4-triaz+ (69)	-321.113681
1,4-dimethyl-1,2,4-triaz+ (70)	-321.128140
1,4-dimethyl-3-nitro-1,2,4-triaz+ (71)	-525.592885

Table A-2.  $H_g(298)$  estimates derived from B3LYP/6-31+G(d,p) results (continued).

<b>Cations</b>	<b><math>H</math> hartrees</b>
<b>1,2,4-Triazolium Cations</b>	
1-amino-4H-1,2,4-triaz+ (72)	-297.854745
4-amino-1H-1,2,4-triaz+ (73)	-297.847293
1-amino-4-methyl-1,2,4-triaz+ (74)	-337.146894
1-methyl-4-amino-1,2,4-triaz+ (75)	-337.143488
1-nitroxymethyl-2-methyl-1,2,4-triaz+ (76)	-600.778216
1-nitroxymethyl-4-methyl-1,2,4-triaz+ (77)	-600.791857
1-methyl-4-nitroxymethyl-1,2,4-triaz+ (78)	-600.787056
<b>Tetrazolium Cations</b>	
1,4H-tetraz+ (79)	-258.534984
2-methyl-1H-tetraz+ (80)	-297.812581
3-methyl-1H-tetraz+ (81)	-297.837675
1-methyl-4H-tetraz+ (82)	-297.834295
1-methyl-2H-tetraz+ (83)	-297.808909
1-methyl-3H-tetraz+ (84)	-297.833973
2-methyl-3H-tetraz+ (85)	-297.814985
1,2-dimethyltetraz+ (86)	-337.109825
1,3-dimethyltetraz+ (87)	-337.135339
1,4-dimethyltetraz+ (88)	-337.131896
2,3-dimethyltetraz+ (89)	-337.115885
1,3,5-trimethyltetraz+ (90)	-376.442143
1-amino-4,5-dimethyltetraz+ (91)	-392.458735
1,5-dimethyl-3-aminotetraz+ (92)	-392.458070
1-nitroxymethyl-2-methyltetraz+ (93)	-616.772932
1-nitroxymethyl-3-methyltetraz+ (94)	-616.791606
1-nitroxymethyl-4-methyltetraz+ (95)	-616.794788
1-methyl-2-nitroxymethyltetraz+ (96)	-616.772613
1-methyl-3-nitroxymethyltetraz+ (97)	-616.795780
2-nitroxymethyl-3-methyltetraz+ (98)	-616.778305
1,3-dimethyl-5-nitroxymethyltetraz+ (99)	-656.098207
5-nitroxymethyl-1,3H-tetraz+ (100)	-577.501722
<b>Guanidinium and Hydrazinium Cations</b>	
guanidinium (101)	-205.692050
1-nitro-1H-guanidinium (102)	-410.138899
nitroxymethylguanidinium (103)	-524.649007
hydrazinium (104)	-112.150096

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