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The Bond Dissociation Energy of the N–O Bond

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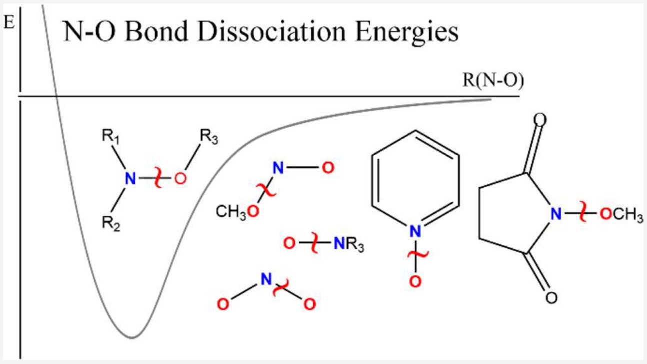
ABSTRACT: Bond dissociation energy (BDE) has been calculated for a series of compounds that contain N–O bonds. These structures encompass model *N*,*N*,*O*-trisubstituted hydroxylamines that include *O*-methoxy, *O*-acyl, and *O*-phenyl hydroxylamines. The calculations used three accurate composite methods, CBS-QB3, CBS-APNO, and G4 methods and the computationally more affordable M06-2X/6-311+G(3df,2p) density functional theory (DFT) functional. The calculated N–O single-bond BDEs are 5–15 kcal/mol higher than a generic N–O BDE of 48 kcal/mol quoted in the literature and in textbooks. The M06-2X DFT functional provides BDEs that are in excellent agreement with the higher-level composite methods. We also provided a comparison of the N–O BDE for pyridine-*N*-oxide to simple trialkylamine oxides. Based on an experimental BDE of 63.3 ± 0.5 kcal/mol for pyridine-*N*-oxide, our best estimate gives 56.7 ± 0.9 kcal/mol N–O BDE for trimethylamine-*N*-oxide and 59.0 ± 0.8 kcal/mol for triethylamine-*N*-oxide.



■ INTRODUCTION

When working with any given class of organic compounds, it is of vital importance from both a synthetic and mechanistic perspective to have an understanding of the relative bond dissociation energy (BDE) of the principal functional groups involved. There are a wide variety of novel compounds that contain the N–O bond, and numerous synthetic examples exist.[1,2] However, very little emphasis has been placed upon measuring the BDE of the N–O bond. It has been suggested that the generic BDE for the N–O single bond in simple compounds such as hydroxylamines averages about 48 kcal/mol, although a number of hydroxylamines have been reported with stronger N–O bonds[3] (55–65 kcal/mol). Historically, experimentally determined bond energies have always been better accepted than theoretically derived values. In contrast, the O–O bonds in peroxides and related oxidants have been the subject of numerous studies with particular emphasis being placed upon the O–O BDE because of its unusual reactivity. Perhaps an exception to that generalization is O–O BDE values where in many cases may be more accurately obtained by computational methods.[4,5] In the present study, we have calculated the N–O BDEs of a series of related N–O containing compounds with high-level composite methods, CBS-QB3, CBS-APNO, and G4, and compared the results with BDEs obtained by the M06-2X density functional theory (DFT) method, which is readily affordable for larger molecules.

■ METHODS

The Gaussian 16 series of programs[6] has several general theoretical methods available that provide thermodynamic data within "chemical accuracy" (ca. 1–2 kcal/mol). The CBS-QB3,[7] CBS-APNO,[8] and G4[9] methods have been shown to provide ΔH and ΔG values that are in very good agreement with experimental values, typically within a 1–2 kcal/mol experiment. For example, the root-mean-square deviations for ΔH and ΔG are 1.06 and 1.14 kcal/mol for the CBS-APNO method, 1.16 and 1.28 for the G4 method, and 1.43 and 1.49 kcal/mol for the CBS-QB3 method, respectively.[10] These theoretical methods have been rank-ordered G4 > CBS-APNO > CBS-QB3 where the CBS-X methods on average predict ΔH_f° within ≈1.2 kcal/mol.[11] In general, CBS-APNO tends to underestimate the formation enthalpies of target molecules whereas CBS-QB3 and G4 have a tendency to overestimate them.[12,13] All molecular orbital calculations were carried out using the Gaussian 16 program system[6] utilizing gradient geometry optimization[14] and harmonic frequency calculations to obtain zero-point energies and thermal corrections for the enthalpies. The bond dissociation enthalpies for the N–O bonds were computed at the CBS-QB3, CBS-APNO, and G4 levels of theory. The W1BD method[15] is an even more

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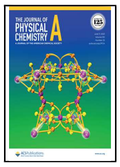

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Table 1. N−O Bond Dissociation Enthalpy (BDE at 298 K) for Selected NO Containing Compounds

NO compounds	M06-2X[a]	CBS-QB3	CBS-APNO	G4	expt
NO	150.19	151.68	150.38	151.13	150.71[b]
NO_2	71.29	74.20	75.10	73.68	73.21[b]
NH_2OH	61.35	60.72	59.79	58.82	
NH_2OCH_3	55.71	56.34	56.11	54.88	
$(CH_3)_2NOH$	63.07	63.89	62.81	61.64	
$(CH_3)_2NOCH_3$	54.22	55.71	55.47	53.97	
$(CH_3)_2NOC(O)CH_3$	58.53	55.62	55.24	53.79	
$CH_3(C{=}O)NHOCH_3$	62.34	61.39	62.26	59.72	
N-methoxysuccinimide	74.14	73.60	73.44	70.03	
$CH_3(Ph)NOCH_3$	45.23	44.90	46.34	44.22	
$(CH_3)_2NOPh$	37.96	36.71	36.90	35.99	
CH_3ONO *anti*	39.01	41.20	42.95	41.11	
CH_3ONO *syn*	40.61	42.27	43.40	41.74	42.5[b,c]
CH_3ONO_2	43.39	42.57	41.99	41.49	42.5[b,c]
pyridine-*N*-oxide	62.56	64.66	63.68	62.98	63.3[d]
Me_3NO	55.70	57.85	56.40	57.06	61.1[e]
Et_3NO	58.90	59.81	58.94	58.31	
average[f]	54.18	54.48	54.38	53.05	

[a]6-311+G(3df,2p) basis set. [b]Ref 18. [c]Ref 17. [d]Ref 20. [e]Ref 21. [f]Excluding NO and NO_2.

accurate level of theory, but computational costs limit its use to smaller molecules. Nitric oxide, nitrogen dioxide, and hydroxylamine were calculated at the W1BD level to obtain more accurate reference values. The BDEs calculated with the M06-2X DFT functional[16] utilized the 6-311+G(3df,2p) basis set. The expectation values of S^2 for the radicals computed with M06-2X were all below 0.80. The calculated BDE values are compared with the available experimental data in Table 1. The structures of the NO compounds described in Table 1 are discussed in the text. In all cases, the reported BDE assumes a simple homolytic N−O bond cleavage. Total energies, enthalpies, and geometric coordinates for individual species are provided either in the text or in the Supporting Information. Except as noted, all total enthalpies shown in the figures were calculated with the G4 method; geometries listed in the figures were calculated at the B3LYP/6-31G(2df,p) level within the G4 calculations.

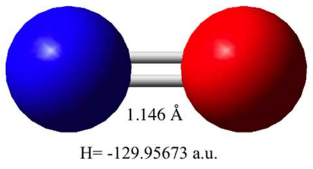
■ RESULTS AND DISCUSSION

To date, there have been very few experimental reports of accurate measurements of the N−O bond energy in complex organic molecules. As accurate theoretical techniques have become more available, the application of computational methods based upon quantum chemistry has been applied to obtain highly accurate bond energies for a variety of functional groups.

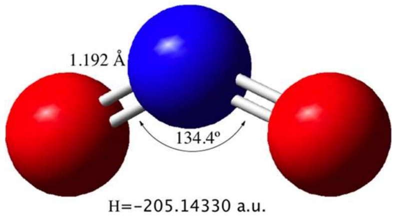
Calculation of the BDE for Nitric Oxide and Nitrogen Dioxide at the W1BD Level. The most fundamental NO bond is that for nitric oxide. The experimental BDE for a generic single N−O bond is reported to be 48 kcal/mol.[3] However, nitric oxide or nitrogen monoxide is a diatomic molecule with a BDE (150.71 kcal/mol) that is intermediate between dioxygen (119.13 kcal/mol) and dinitrogen (225.83 kcal/mol).[17] It is one of the principal oxides of nitrogen and exists as a free radical since it has an unpaired electron and is consequently often denoted as its dot formula (·N═O or ·NO). Because of this rather special bonding arrangement, we applied a higher level of theory and found the W1BD composite method to give a BDE of 149.99 kcal/mol, in excellent agreement with an experimental value of 150.71 kcal/mol (Table 1). The CBS-QB3, CBS-APNO, and G4 methods agree equally well with the experiment. We have recently reported that the M06-2X functional with a large basis set can provide O−O BDEs, in very good agreement with higher-level composite methods. As noted in Table 1, the M06-2X functional is also in excellent agreement with the experimental values and with the higher-level composite methods.

We have also included nitrogen dioxide at the W1BD level of theory to provide an accurate reference level for comparison to the other methods that we have included. Its ground state is a doublet since nitrogen has one unpaired electron, and this creates a relatively weak bond with the oxygen lone pairs so the formula for nitrogen dioxide is often written as a dot formula $\cdot NO_2$, consistent with its free radical status. The weakness of the N−O bond suggests that this compound would be a good oxidizing agent, and it does combust with compounds such as hydrocarbons. Calculations with the spin-unrestricted M06-2X level of theory provide a better value for the BDE (71.29 kcal/mol) than the spin-restricted open shell M06-2X (69.82 kcal/mol) compared to the experiment (73.21 kcal/mol,[18] see Table 1). The W1BD method gives a N−O BDE of 73.42 kcal/mol, in excellent agreement with an experimental value. Unrestricted W1BD calculations show the N−O bond in NO_2 to be noticeably weaker than that in NO (ΔBDE = 77.32), although the N−O bond distances in both compounds are quite similar (Figure 1). All of the composite methods provide a N−O BDE within 1 kcal/mol except for the CBS-APNO method that is 1.9 kcal/mol higher, while the UM06-2X method provides a N−O bond energy that is lower by the same amount.

Comparison of the N−O BDEs Calculated with CBS-QB3, CBS-APNO, G4, and DFT. Substituted hydroxylamines have recently been explored as an emerging functional group that has potential in medicinal chemistry. Particular emphasis has been placed upon new synthetic methods for *N*,*N*,*O*-trisubstituted hydroxylamines.[22] We initiate this study by examining the N−O BDE for relatively small N−O containing examples that simplify the computational requirements. Hydroxylamine is the simplest single N−O bond compound in this class of inorganic structures (Figure 2). It is a white



Nitric Oxide



Nitrogen Dioxide

Figure 1. Nitric oxide and nitrogen dioxide at the W1BD level of theory.

crystalline hygroscopic solid that is unstable and decomposes at room temperature or when dissolved in hot water. It should be stored at 10 °C, and this obviously puts a serious demand on the accurate experimental measurement of its N−O BDE. Consequently, this BDE may be obtained more accurately by computational methods. The W1BD method yields a BDE of 59.91 kcal/mol, which can serve as a reference value in the absence of a directly measured experimental value. The 61.35 kcal/mol BDE for hydroxylamine with the M06-2X functional is within 1.5 kcal/mol (Table 1) of the W1BD method, while the CBS-QB3, CBS-APNO, and G4 methods are within 1 kcal/mol, providing excellent agreement for all of the methods employed.

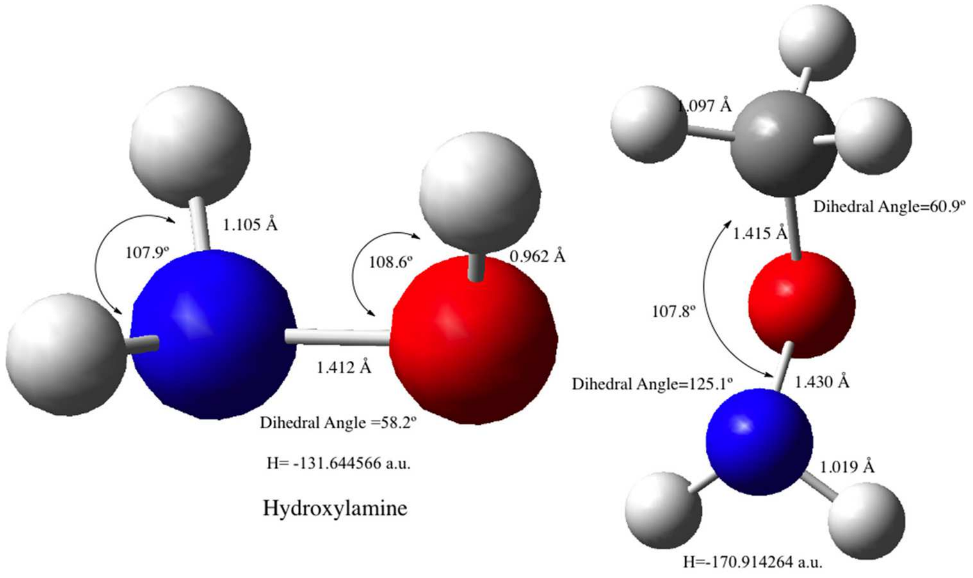
As we noted in a recent study on peroxides,[5] the often quoted O−O BDE in the generic literature (34 kcal/mol) is about 11 kcal/mol lower than what we found by computational means. Similarly, the generic N−O single-bond BDE is quoted to be 48 kcal/mol,[3,19] which is 5−15 kcal/mol lower than the BDEs obtained by computational means in our study.

Next, we examined a set of simple methyl-substituted hydroxylamines: methoxyamine, *N*,*N*-dimethylhydroxylamine, and *N*,*N*-methylmethoxyamine. Methoxyamine hydrochloride is a commonly used reagent for the generation of oxime derivatives of aldehydes and ketones. We observe a reduction of 4 kcal/mol in the N−O BDE for methoxyamine compared to hydroxylamine (Table 1). The difference is 6 kcal/mol with M06-2X.

N,*N*-Dimethylhydroxylamine is a commonly used reagent in organic synthesis. We see a small increase compared to NH_2OH (3 kcal/mol for the composite methods, 2 kcal/mol for M06-2X). The addition of a methoxy substituent in *N*,*N*-dimethylmethoxyamine (Figure 3) results in a 7−9 kcal/mol reduction in the N−O BDE, compared to a 4−6 kcal/mol reduction found for methoxyamine compared to hydroxylamine. An experimental BDE (48 kcal/mol) has been reported for *N*,*N*-dimethylmethoxyamine, but this was estimated by using bond additivity methods.[19] When an acyl group is attached to the *N*,*N*-dimethylhydroxylamine oxygen atom, the reduction in the N−O BDE is 5−8 kcal/mol (Table 1).

As noted above for our previous study on the O−O bond BDE,[5] we utilized the 6-311+G(3df,2p) basis set for all of the M06-2X DFT calculations reported. This protocol provided BDEs that are in excellent agreement with the higher-level CBS-QB3, CBS-APNO, and G4 composite methods, and this allows one to calculate bond energies in fairly large molecules that may be out of reach for more computational demanding higher-level methods. When we used the less flexible 6-311+G(d,p) basis set for dimethylmethoxyamine, the M06-2X BDE dropped from 54.22 to 53.12 kcal/mol. However, when the basis set was further reduced to 6-31G(d), we observed an increase in the BDE to 56.79 kcal/mol, demonstrating the fact that a fairly large flexible basis set is essential to get reliable bond energies with the M06-2X DFT method.

We next turned our attention to the effect of carbonyl groups on the BDE of the N−O bond. A carbonyl group



Hydroxylamine

Methoxyamine

Figure 2. Hydroxylamine and methoxyamine at the G4 level of theory.

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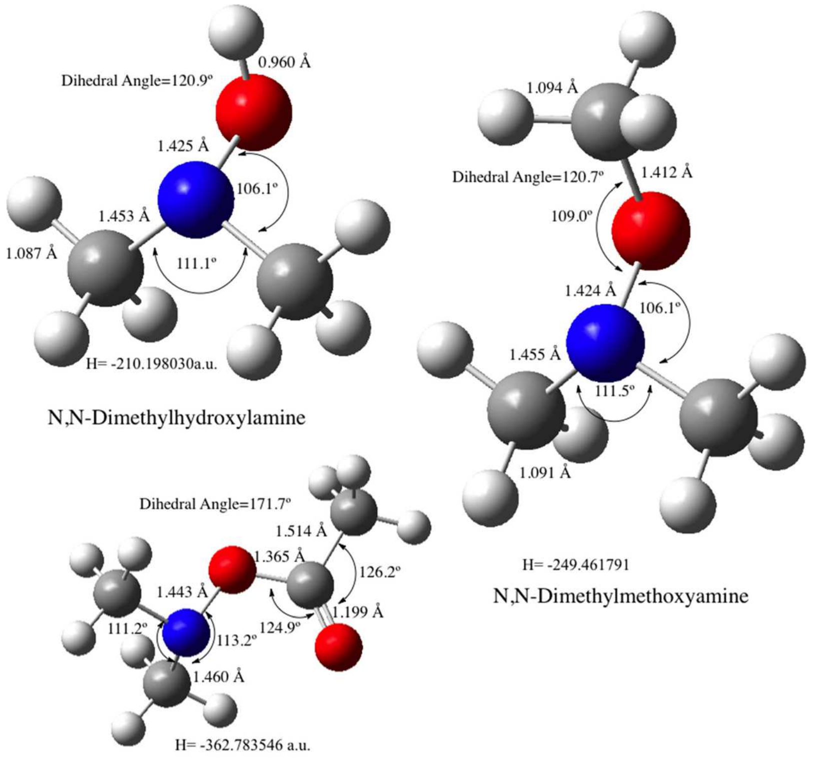
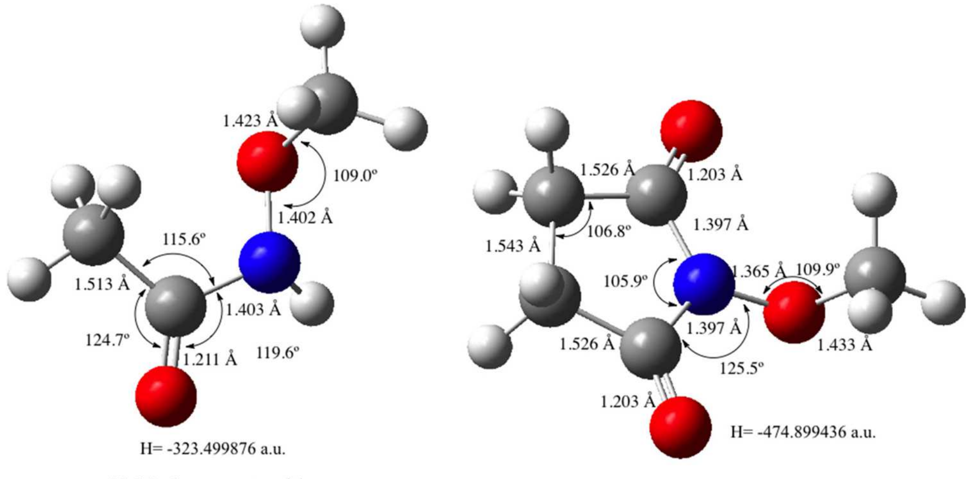


N,N-Dimethylhydroxylamine

N,N-Dimethylmethoxyamine

N,N-Dimethyl-O-acylhydroxylamine

Figure 3. *N*,*N*-Dimethylhydroxylamine, *N*,*N*-dimethylmethoxyamine, and *N*,*N*-dimethyl-*O*-acylhydroxylamine at the G4 level of theory.



N-Methoxyacetamide

N-Methoxysuccinimide

Figure 4. *N*-Methoxyacetamide and *N*-methoxysuccinimide at the G4 level of theory.

adjacent to the oxygen atom, as in $(CH_3)_2NOC(O)CH_3$, has very little effect on the N−O BDE compared to $(CH_3)_2NOCH_3$ when computed with CBS-QB3, CBS-APNO, and G4. By contrast, the presence of one C═O adjacent to the nitrogen atom has a significant effect. The BDE for *N*-methoxyacetamide (Figure 4) is 5−6 kcal/mol higher than methoxyamine, suggesting that the resonance interaction of an acyl group with the nitrogen atom is the source of the increase in the BDE. To that end, we investigated the effect of two carbonyl substituents on the nitrogen atom in *N*-methoxysuccinimide and observed a 15−17 kcal/mol increase in the BDE relative to that of methoxyamine with CBS-QB3, CBS-APNO, and G4. With M06-2X, the increase in the N−O BDE was 19 kcal/mol. The average BDE for the four methods is the highest BDE that we report (72.8 kcal/mol), reflecting the inductive effect of the carbonyl groups.

Since the resonance interaction of a carbonyl group on the N atom had a profound effect upon the BDE of an adjacent N−O bond, we elected to examine the role of a phenyl group. We compared the relative N−O BDE of a N-phenyl group to the N−O bond energy of *N*,*N*-dimethylmethoxyamine (Figure 5). The BDE for methyl(phenyl)methoxyamine is 9−11 kcal/mol lower than dimethylmethoxyamine, which can be attributed to the N atom lone pair resonance interaction with the phenyl ring. The effect is twice as large when the phenyl group is substituted on the oxygen atom, resulting in a

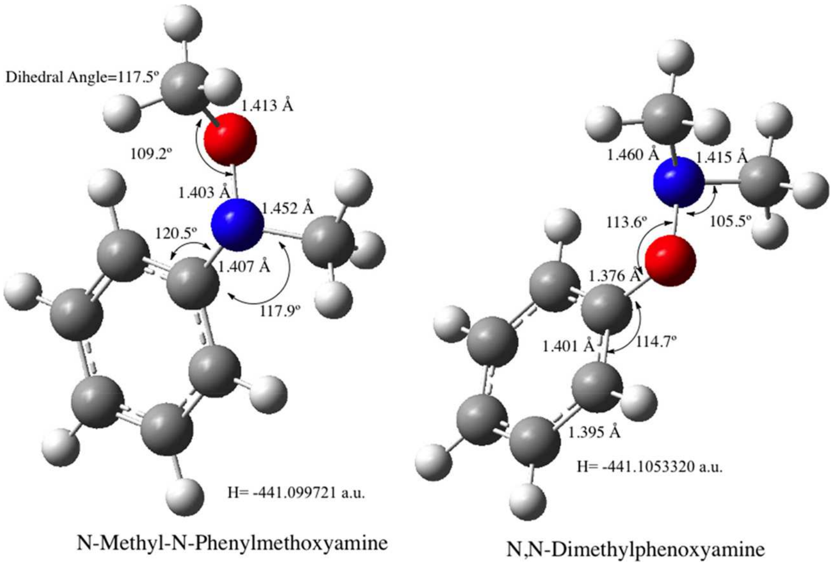


Figure 5. *N*-Methyl-*N*-phenylmethoxyamine and *N*,*N*-dimethylphenoxyamine at the G4 level of theory.

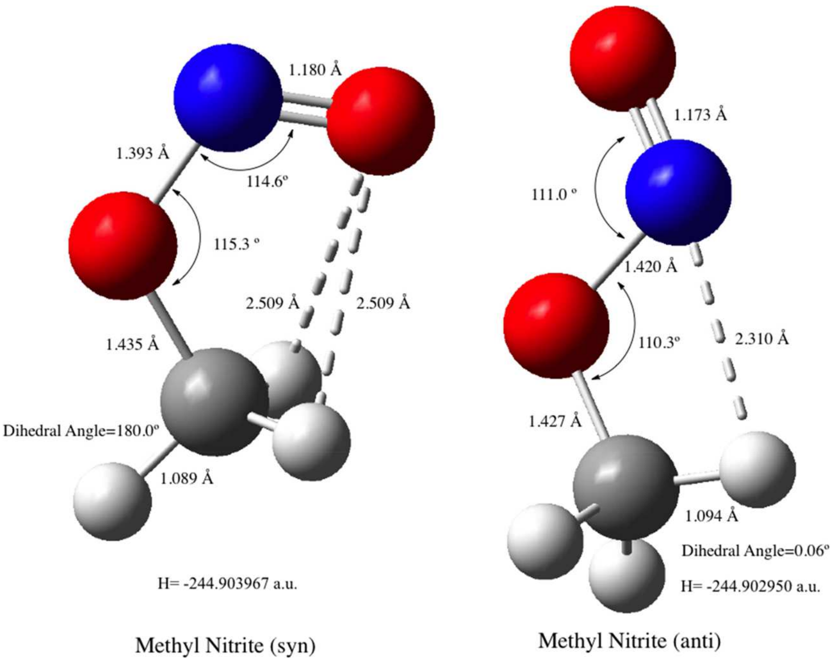


Figure 6. Methyl nitrite *syn* and *anti* at the G4 level of theory.

BDE for $(CH_3)_2N$–O-phenyl that is 16–19 kcal/mol lower than that for $(CH_3)_2NOCH_3$. Cleaving the N–O-phenyl bond produces the PhO· free radical where the radical is stabilized by resonance and delocalized over the entire system, thereby lowering the N–O bond BDE. We note that, when the O–O bond cleavage produces the phenoxy radical, the corresponding BDE is also reduced markedly.[5] In contrast, when the N–O bond is broken and the nitrogen atom is attached to an acyl group as in *N*,*N*-dimethyl-*O*-acylhydroxylamine (Figure 3), the acetyloxy radical is formed that is slightly more inductive than a methoxy group, potentially resulting in an increase in the N–O BDE. In general, when C=O is bonded directly to the nitrogen atom, as noted in *N*-methoxyacetamide, the N–O bond BDE increases due to the delocalization of the nitrogen lone pair. The effects of the spin contamination in the PhO· radical and PhNMe radical were checked by calculating the BDEs with spin-restricted open shell calculations. The ROM06-2X BDEs are 3–4 kcal/mol higher than the UM06-2X BDEs, but the latter are in better agreement with CBS-QB3, CBS-APNO, and G4. The CBS-QB3 BDEs changed by less than 0.5 kcal/mol when calculated with a spin-restricted open shell approach. Because the composite methods are based on coupled cluster calculations, they tend to be less sensitive to modest amounts of spin contamination. The BDEs calculated by CBS-QB3, CBS-APNO, and G4 should be affected by less than 1 kcal/mol.

Another interesting and very important class of N–O containing compounds includes high-energy explosives such as nitromethane, methyl nitrite, and methyl nitrate. Methyl nitrite is a heat-sensitive gaseous explosive that has been used as rocket fuel. It exists as a mixture of *cis* and *trans* isomers with the former being favored by only 0.5–1.6 kcal/mol (Figure 6).

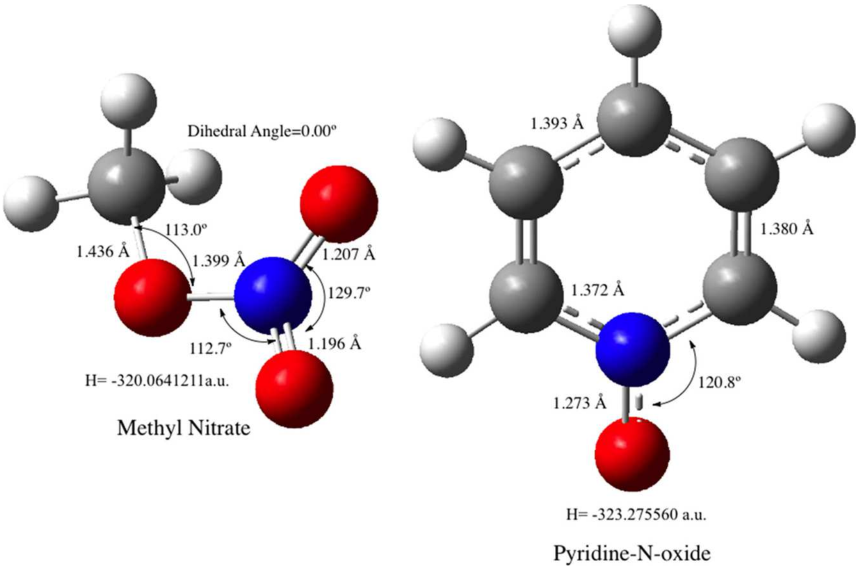


Figure 7. Methyl nitrate and pyridine-*N*-oxide at the G4 level of theory.

It is worth noting that the *syn* isomer has two hydrogen atoms hydrogen-bonded to the N═O oxygen atom (2.509 Å), while the *trans* isomer has a single slightly stronger hydrogen bond to the nitrogen atom (2.310 Å) that could explain their relatively small energy differences (Figure 6). Methyl nitrite is a particularly interesting example because the N−O bond cleavage affords ·N═O with its unpaired electron. The more stable *cis* isomer has an experimental BDE of 42.5 kcal/mol;[17,18] the composite methods are all within 1 kcal/mol of this value, while M06-2X is within 2 kcal/mol.

Methyl nitrate is a colorless volatile liquid that is a very strong explosive. As anticipated, the BDE for methyl nitrate (Figure 7) also has a relatively low N−O bond energy (42.5 kcal/mol)[17,18] that is characteristic of all such explosive materials. The BDEs calculate with M06-2X, and the composite methods are all within 1 kcal/mol of the experimental value.

One of the more unusual heterocyclic compounds that has a N−O bond is pyridine-*N*-oxide (Figure 7). This is a planar molecule that arises from the oxidation of pyridine. Its stable dipolar ambivalent nature makes it much more reactive in a variety of ways relative to its parent pyridine. As a result of the charge separation in its N−O bond, with a charge on oxygen of about −0.6e, it can undergo reactions with both nucleophilic and electrophilic reagents. The calculated BDE (62.56−64.66 kcal/mol) shows that this is a relatively stable N−O bond despite its high and unusual reactivity. The M06-2X, G4, and CBS-APNO BDEs are within 1 kcal/mol of the experimental value, while the CBS-QB3 BDE is 2.1 kcal/mol higher.

The experimental BDE for pyridine-*N*-oxide has been a matter of some controversy. Amine oxides are very hygroscopic crystalline compounds that are difficult to purify, which makes an accurate determination of its standard molar enthalpy of formation difficult. These experimental difficulties impact the application of combustion calorimetry and thus the accuracy of its N−O BDE. This is another prime example of where computational methods can provide more reliable bond energies. For example, the earlier N−O BDE for pyridine-*N*-oxide reported by Pilcher and Shaofeng[23] (72.1 kcal/mol) was quite high but was later corrected and a consensus value of 63.3 kcal/mol[20] is in excellent agreement with our CBS-APNO and G4 values (Table 1).

The N−O BDEs for a number of substituted pyridine-*N*-oxides have also been reported, and it has been shown that the presence of substituents on the pyridine ring does not impact the N−O BDE of a series of pyridine-*N*-oxides that seem to remain within a relatively narrow range of 62.1 ± 2.4 kcal/mol.[20,24] We also examined the reactivity of *N*-methoxypyridine (not shown) and were surprised to find that it has a negative BDE of −14.98 kcal/mol and readily dissociates into pyridine and the methoxy radical. The methoxy pyridine adduct has the unpaired electron in the π*-orbital of the pyridine ring, reducing the aromaticity and destabilizing methoxy pyridine relative to pyridine and the methoxy radical. This also provides a plausible explanation for why attempted alkylation of pyridine-*N*-oxide results in C2-alkylation.[25,26] Another example of a weakened N−O bond involving resonance stabilization has recently been reported for the unknown nonaromatic *N*-methylpyrrole-*N*-oxide. This N-oxide, if it could exist with such a weak N−O bond, has a calculated N−O BDE of only 13−18 kcal/mol since N−O bond dissociation yields the aromatic *N*-methylpyrrole with a resonance energy of 24−27 kcal/mol.[27]

It is also of interest to compare the relative N−O BDE of pyridine-*N*-oxide to that of simple trisubstituted amine oxides. Intuitively, it would seem that these two classes of amine oxides should have different N−O BDEs because of the aromatic nature of the former. As we have observed above, there is no reliable experimental data for simple amine oxides that can be applied to the determination of accurate BDEs. Trimethylamine oxide is an important biological compound that has many functions in both human and marine animal life. An experimental N−O BDE for trimethylamine oxide has been assigned (61.1 kcal/mol) using some necessary assumptions. However, the corresponding computational methods (M06/6-311G+(d,p)) gave a BDE that was 5.6 kcal/mol lower.[21] We observe a N−O BDE of 55.7 kcal/mol with our somewhat more flexible basis set M06-2X/6-311+G(3df,2p) that is essentially identical with this value. The BDEs for the composite methods are in general agreement with the G4 value being 1.4 kcal/mol higher (Table 1). The isodesmic

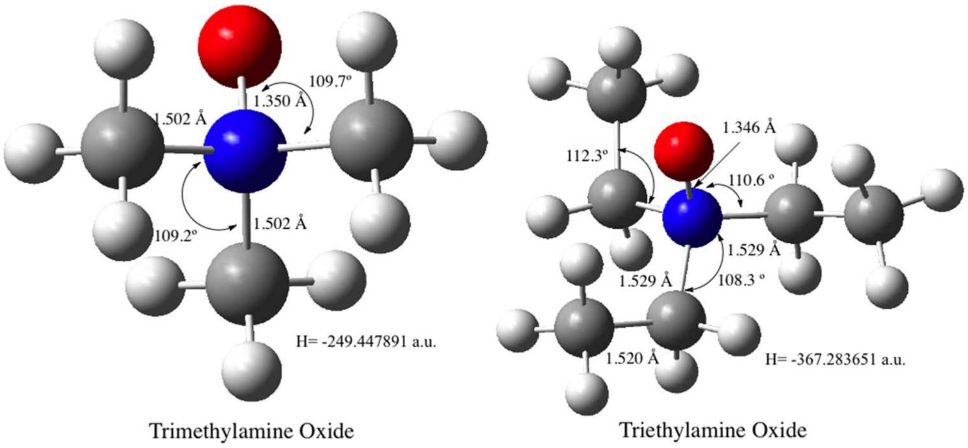


Figure 8. Trimethylamine oxide and triethylamine oxide at the G4 level of theory.

reaction formed by taking the difference in the BDEs of pyridine oxide and trimethylamine oxide should be more accurate than the individual BDEs because of the cancellation of errors.

$$(CH_3)_3NO + \text{pyridine} \rightarrow (CH_3)_3N + \text{pyridine-}N\text{-oxide} \quad (1)$$

All four methods fall in the range of 6.6 ± 0.7 kcal/mol. Combined with an experimental BDE of 63.3 ± 0.5 kcal/mol for pyridine-*N*-oxide gives 56.7 ± 0.9 kcal/mol as our best estimate of the experimental N−O BDE of trimethylamine-*N*-oxide. Likewise, the BDE for triethylamine oxide, the isodesmic reaction

$$(C_2H_5)_3NO + \text{pyridine} \rightarrow (C_2H5)_3N + \text{pyridine-}N\text{-oxide} \quad (2)$$

has an average heat of reaction of 4.3 ± 0.6 kcal/mol, which gives 59.0 ± 0.8 kcal/mol as our best estimate of the experimental N−O BDE of triethylamine-*N*-oxide.

The coordinate-covalent bonding between the donor nitrogen and the acceptor oxygen in amine oxides is atypical in nature. In pyridine-*N*-oxide, a portion of the negative charge can be delocalized back into the aromatic ring. For example, the N−O bond distance in pyridine-*N*-oxide (1.273 Å) is 0.073 Å shorter than that in triethylamine oxide; the N−O bond distance in triethylamine oxide is essentially the same as that in trimethylamine oxide (Figure 8). The average N−O distance for normal covalent bonds in the above compounds in Figures 2−6 is 1.414 Å, supporting the contention that amine oxides do have shorter N−O distances due to coordinate-covalent bonding. Electron withdrawing groups such as C═O do tend to result in shorter N−O bonds but only by 0.02−0.05 Å, as shown in *N*-methoxysuccinimide and methyl nitrate.

■ CONCLUSIONS

Three high-level composite methods were used to calculate the N−O BDEs of a representative set of N−O compounds. Similar to O−O BDEs, we again see that the M06-2X DFT method provides BDEs that are in very good agreement with the higher-level composite methods. The average N−O value for the 15 compounds in Table 1 with the M06-2X DFT functional is 54.18 kcal/mol. The average N−O BDE values at the CBS-QB3 and CBS-APNO levels are essentially identical at 54.48 and 54.38 kcal/mol, respectively. The G4 BDE values on average are 1.4 kcal/mol lower than the other composite methods. The overall average of all four methods is 53.97 kcal/mol, and without the M06-2X functional, the average is 54.02 kcal/mol. The overall agreement between the four methods convincingly demonstrates that the M06-2X functional can be used to accurately ascertain the dissociation enthalpy for the N−O bond and that it is economically feasible to apply to relatively large molecules. We suggest that the generic value for the average N−O bond is 54 kcal/mol. The N−O BDEs differ by as much as 36 kcal/mol for just the 15 molecules included in this study. The observed BDE can be reduced by the formation of a PHO· radical or even ·NO itself. The conjugation effects of a carbonyl group adjacent to the nitrogen atom can markedly increase the N−O bond dissociation enthalpy. The BDE averaged over all four methods suggests that the BDEs for trimethylamine oxide and triethylamine oxide are 6.7 and 4.5 kcal/mol lower than the BDE of pyridine-*N*-oxide.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpca.1c02741.

Total energies and Cartesian coordinates for all structures (PDF)

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Notes

The authors declare no competing financial interest.

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