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The evaluation of bond dissociation energies for NO_2 scission in nitro compounds using density functional and complete basis set methods*

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By using the density functional theory (B3LYP) and four highly accurate complete basis set (CBS-Q, CBS-QB3, CBS-Lq, and CBS-4M) ab initio methods, the X(C, N, O)–NO_2 bond dissociation energies (BDEs) for CH_3NO_2, $C_2H_3NO_2$, $C_2H_5NO_2$, $HONO_2$, CH_3ONO_2, $C_2H_5ONO_2$, NH_2NO_2 $(CH_3)_2NNO_2$ are computed. By comparing the computed BDEs and experimental results, it is found that the B3LYP method is unable to predict satisfactorily the results of bond dissociation energy (BDE); however, all four CBS models are generally able to give reliable predication of the X(C, N, O)–NO_2 BDEs for these nitro compounds. Moreover, the CBS-4M calculation is the least computationally demanding among the four CBS methods considered. Therefore, we recommend CBS-4M method as a reliable method of computing the BDEs for this nitro compound system.

Keywords: bond dissociation energy, B3LYP, CBS models, nitro compound
PACC: 3520G, 3120A, 3600

1. Introduction

The stability and impact/shock sensitivity of energetic materials have frequently been related to the strength of C–NO_2 and/or N–NO_2 bonds.[1−6] Moreover, the bond strength may be obtained by calculating the bond dissociation energy. For designing and evaluating new energetic compounds, it is accordingly important to be able to determine computationally the dissociation energies of these bonds. This is complicated, however, by the well-known difficulties involved in describing the electronic structures of nitro compounds.[7−11]

The necessity of using a high level of theory coupled with the size of many energetic molecules makes the highly accurate complete basis set (CBS) ab initio or the hybrid B3LYP functional approach a possible computational option. In the present work, we investigate the effectiveness of four different CBS (CBS-Q, CBS-QB3, CBS-Lq, and CBS-4M) and B3LYP methods in reproducing the C-NO_2 BDEs and the selected equilibrium bond distances in CH_3NO_2, $C_2H_5NO_2$ nitro compounds, which are well known for their use in ammunition as liquid explosives,[12,13] and the N–NO_2 BDE and bond distance in $(CH_3)_2NNO_2$ compound, which is a prototype of modern explosives, such as RDX (hexahydro-1,3,5-trinitro-s-triazine). In the meantime, we have included the C–NO_2 bond for $C_2H_3NO_2$, the O–NO_2 BDE for $HONO_2$, CH_3ONO_2, and $C_2H_5ONO_2$, the N–NO_2 bond for NH_2NO_2 in this study.

2. Computational methodology

All computation studies were performed with the GAUSSIAN 98[14] package with the CBS-4M, CBS-Lq, CBS–QB3, and CBS–Q ab initio and B3LYP density functional theory (DFT) methods implemented in the computational package. The hybrid B3LYP[15] DFT method has the form $A.E_X^{\text{Slater}} + (1\text{-}A).E_X^{\text{HF}} +$

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B.$\Delta E_X^{\text{Becke}} + E_C^{\text{VWN}}$+ C.$\Delta E_C^{\text{non-local}}$, where the non-local correlation is provided by the LYP[16] expression. In this equation, Slater is provided by the Slater exchange functional,[17] the constants A, B and C are those determined by Becke which fit into the G1 molecular set and VWN is from the Vosko–Wilk–Nusair expression.[18]

The highly accurate level CBS method developed by Petersson and co-workers,[19−22] which is defined to include corrections for basis set truncation errors, uses double zeta plus polarization level atomic pair natural orbital basis sets to calculate molecular self-consistent-field (SCF) energies and correlation energies. The energy of the chemical system is computed from a series of calculations. The complete basis set-quadratic configuration interaction (CBS-Q)[19−23] ab initio model starts with a zero point energy computed and a geometry optimization on the Hartree–Fock theory, in which the geometry is further optimized on the second order of Møller–Plesset (MP2) theory. Then the energy is evaluated with MP2 theory with a larger basis set and a CBS extrapolation to correct the energy through the second order. Two additional calculations are used to approximate higher orders of contributions [MP4(SDQ)/6-31+G†† and QCISD(T)/6-31+G†]. There are also empirical corrections for spin contamination and a size-consistent higher-order correction.

The CBS-QB3 model[23−25] combines the general design of the CBS-Q energy calculation with B3LYP DFT optimized geometries and frequencies. The model begins with a geometry optimization and a zero point energy computed on the B3LYP theory. Like the above CBS-Q procedure, then the energy is evaluated with MP2 theory with a larger basis set and a CBS extrapolation to correct the energy through the second order. The MP4(SDQ)/6-31+G(d') and CCSD(T)/6-31+G(d') calculations are used to approximate higher orders of contribution. Empirical corrections for spin contamination and a size-consistent higher-order correction are also considered.

As for the CBS-4M[23−25] model, first, a geometry optimization and a zero point energy computed are carried out on Hartree–Fock theory. Then the energy is evaluated with the second order of Møller–Plesset (MP2) theory with a larger basis set and a CBS extrapolation to correct the energy through the second order. The MP4SDQ/6-31G calculation is used to approximate higher orders of contributions. There are also empirical corrections for spin contamination and a size-consistent higher-order correction.

The CBS-Lq[21,23] model is very similar to the CBS-4M model, using identical geometry, zero point energy, and CBS2 energy components, it differs only in the treatment of higher-order correlation energy and the empirical corrections. The higher-order contributions are calculated with the same MP4(SDQ) and QCISD(T) methods as the CBS-Q calculation, but with much smaller basis sets.

Of the above four CBS models considered, the accuracy of results usually increases from low to high in the order CBS-4M< CBS-Lq< CBS–Q< CBS–QB3.

3. Results and discussion

The X(C, N, O)-NO_2 BDEs for CH_3NO_2, $C_2H_3NO_2$, $C_2H_5NO_2$, $HONO_2$, CH_3ONO_2, $C_2H_5ONO_2$, NH_2NO_2, and $(CH_3)_2NNO_2$ nitro compounds are predicted, using the B3LYP with 6-311G** and 6-311+G** basis sets, CBS-4M, CBS-Lq, CBS–QB3, and CBS–Q methods. The calculation results and the experimental data taken from Ref.[26] are presented in Table 1. It can be noticed that, although the hybrid B3LYP method is a popular computational tool, which produces an extraordinary agreement between the computed and experimental energies and properties for some polar molecules,[27−29] it gives rather poor BDE for the nitro compounds. As we can see, the X(C, N, O)–NO_2 BDEs computed with the B3LYP at 6-311G** and 6-311+G** basis sets for these nitro compounds are substantially lower than the corresponding experimental values. The B3LYP with 6-311G** and 6-311+G** basis sets produces in average absolute differences of 28.81×10^3 and 34.13×10^3J mol^{-1}, respectively, which exceed our desired target accuracy for chemical prediction. Therefore the B3LYP/6-311G** and B3LYP/6-311+G** computation methods are unable to predict the satisfactory X(C, N, O)–NO_2 BDEs for the studied nitro compounds.

Table 1. The BDEs (10^3J mol^{-1}) at 298K for X(C,N,O)–NO_2 nitro compounds using the B3LYP with 6-311G** and 6-311+G** basis sets and various CBS theory methods.

	B3LYP[a)]	B3LYP[b)]	CBS-QB3	CBS-4M	CBS-Lq	CBS-Q	Exp.[c)] at 298K
CH_3–NO_2	219.83	221.79	254.93	250.58	245.06	249.58	254.4
C_2H_3–NO_2	263.13	262.17	297.23	290.79	278.61	290.50	299.2
C_2H_5–NO_2	220.41	219.79	260.66	253.05	244.93	254.39	254.4
HO–NO_2	186.23	174.68	206.69	195.89	196.94	202.67	206.3
CH_3O–NO_2	144.35	133.55	178.61	173.72	174.05	177.31	172.4±4.2
C_2H_5O–NO_2	138.74	129.24	178.82	173.34	174.51	177.44	171.5±4.2
NH_2–NO_2	194.97	189.70	216.56	205.27	198.15	213.72	–
$(CH_3)_2N$–NO_2	167.15	161.34	202.67	194.22	186.94	200.37	183.3

[a)] The 6-311G** basis set is used and a zero-point corrected energy is considered.
[b)] The 6-311+G** basis set is used and a zero-point corrected energy is considered.
[c)] The data are taken from Ref.[26].

The CBS methods were previously reported by Montgomery and co-workers[24,25] to be highly accurate and the CBS-Lq and CBS-Q models were ever found to have mean absolute deviations of 7.1×10^3 and 4.2×10^3J mol^{-1}, respectively, for the G2 test set, the CBS-4M and CBS-QB3, 13.64×10^3 and 5.06×10^3J mol^{-1}, respectively, for the G2/97 test set. In the paper, the X(C,N,O)–NO_2 BDE values computed with the CBS-4M, CBS-Lq, CBS–QB3, and CBS–Q methods are listed in Table 1. It is seen that the four CBS methods can generally predict the satisfactory X(C,N,O)-NO_2 BDEs for the studied nitro compounds. We find that the BDEs calculated using the CBS-4M, with an average absolute deviation of 5.44×10^3J mol^{-1}, are in extraordinarily good agreement with the experimental values The largest discrepancies are found for $(CH_3)_2NNO_2$ (10.92×10^3J mol^{-1}), $HONO_2$(10.41×10^3J mol^{-1}), and $C_2H_3NO_2$(8.41×10^3J mol^{-1}). In Table 1, it can be shown that the average absolute deviation from experiment for CBS-QB3 theory is 6.01×10^3J mol^{-1}, while CBS-Q theory is only slightly less accurate, with a mean absolute deviation of 6.44×10^3 J mol^{-1} for the X(C,N,O)-NO_2 BDE of the nitro compounds. The mean absolute deviation between the CBS-Lq and experiment is 8.15×10^3J mol^{-1}, which is somewhat larger than for the other CBS methods. The largest discrepancies for CBS-Lq, in Table 1, are 20.59×10^3J mol^{-1} (for the BDE of C_2H_3–NO_2), 9.47×10^3J mol^{-1} (for the BDE of C_2H_5–NO_2), 9.36×10^3 J mol^{-1} (for the BDEs of HO–NO_2). Although the average absolute error for CBS-Lq is larger than the other CBS methods, in Table 1, the smallest difference for the BDE of $(CH_3)_2N$–NO_2 (within 3.64×10^3J mol^{-1} of the experimental value) is yielded by the CBS-Lq model.

So the high accuracy of the four CBS ab initio approaches is further supported, in this paper. Although the mean absolute difference for the CBS-Lq method is somewhat larger than those found for CBS-Q and the difference for the latter is slightly larger than for CBS-QB3, and the smallest average absolute deviation found for CBS-4M in these compounds is 5.44×10^3J mol^{-1}. So each CBS method considered here is able to produce energies with an average error of 4.2×10^3-8.4×10^3J mol^{-1} for the nitro compounds when compared with the available experimental values.

In Table 2, the equilibrium bond distances computed using the above methods for selected bond in CH_3NO_2, $C_2H_3NO_2$, $C_2H_5NO_2$, $HONO_2$, CH_3ONO_2, $C_2H_5ONO_2$, NH_2NO_2, $(CH_3)_2NNO_2$ molecules, together with the available experimental values, are listed. Because the bond lengths for the CBS-QB3 method are equal to those found for B3LYP/6-311G**, due to the CBS-QB3 calculation starting at the B3LYP/6-311G** optimized structure, only the bond length results with CBS-QB3 computation method are listed in the Table 2. In addition, owning to both the CBS-4M and CBS-Lq methods using the same model for geometry optimization, only the former bond lengths are presented. In the Table 2 it is found that the bond lengths for the CBS-Q are generally closer to the experimental values than the other computation methods.

Table 2. The X(C,N,O)-NO_2 bond lengths (nm) for the many nitro compounds at various levels of theory.

	CBS-QB3	B3LYP[a)]	CBS-4M	CBS-Q	Exp.
CH_3–NO_2	0.1504	0.1503	0.1494	0.1493	0.1488[b)]
C_2H_3–NO_2	0.1473	0.1472	0.1453	0.1468	–
C_2H_5–NO_2	0.1521	0.1519	0.1508	0.1507	–
HO–NO_2	0.1415	0.1417	0.1414	0.1406	–
CH_3O–NO_2	0.1424	0.1422	0.1405	0.1414	0.1402[c)]
C_2H_5O–NO_2	0.1423	0.1419	0.1404	0.1413	0.1407[d)]
NH_2–NO_2	0.1396	0.1393	0.1354	0.1401	0.1427(±0.0002)[e)]
$(CH_3)_2N$–NO_2	0.1387	0.1384	0.1341	0.1397	0.1382(±0.0003)[f)]

[a)] The 6-311+G** basis set is used. [b)] The data taken from Ref.[30]. [c)] The data taken from Ref.[31].
[d)] The data taken from Ref.[32]. [e)] The data taken from Ref.[33]. [f)] The data taken from Ref.[34].

For the computed C–NO_2 bond distances for CH_3NO_2, the results from the CBS-4M method (0.1494 nm) and from CBS-Q (0.1493 nm) are very close to the experimental value (0.1488 nm).[30] The calculated CH_3O–NO_2 bond length at CBS-4M model (0.1405 nm) is in extraordinarily good agreement with the experimental value (0.1402 nm).[31] For the computed C_2H_5O–NO_2 bond length, it is noted that CBS-4M calculation predicts the most accurate result (within 0.0003 nm of the experimental value[32]). We also find that the NH_2–NO_2 bond distance computed with CBS-Q (0.1401 nm) is closer to the experimental value (0.1427±0.0002 nm)[33] than the other methods quoted in the table. The $(CH_3)_2N$–NO_2 bond distance come from B3LYP/6-311+G** (0.1384 nm) is in extraordinarily good agreement with the experimental one (0.1382±0.0003 nm).[34]

4. Conclusion

In conclusion, we can say that all of the CBS ab initio computational methods considered here are substantially superior to the B3LYP with 6-311G** or 6-311+G** basis sets DFT method for computing the X(C, N, O)–NO_2 BDE of the studied nitro compounds. The CBS-4M, CBS-Lq, CBS-QB3, and CBS-Q methods can generally produce the satisfactory results of BDE for the studied system, which have an average error of 4.2×10^3-8.4×10^3J mol^{-1} when compared with the experimental values. The CBS-4M method is able to predict the X(C, N, O)–NO_2 BDEs with almost the same accuracy as do the other three CBS methods. Moreover, the CBS-4M calculation is by far the least computationally demanding among the considered four CBS methods. Therefore, for removal of the NO_2 group for small- and medium-sized molecular system of nitro compound, we recommend CBS-4M method as a reliable method of computing the BDEs.

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