Theor Chem Acc (2011) 130:153–160
DOI 10.1007/s00214-011-0944-6

REGULAR ARTICLE

An examination of density functionals on aldol, Mannich and α-aminoxylation reaction enthalpy calculations

Raman K. Singh · Takao Tsuneda · Kimihiko Hirao

Received: 15 February 2011 / Accepted: 15 April 2011 / Published online: 4 May 2011

Abstract The reaction enthalpies of aldol, Mannich and α-aminoxylation reactions were calculated by density functional theory (DFT) using long-range-corrected (LC), hybrid B3LYP and other up-to-date functionals to show why conventional DFT including B3LYP has given poor enthalpies for these reactions. As a result, we found that long-range exchange interactions significantly affect the reaction enthalpies. We therefore proposed that the poor enthalpies of B3LYP are due to its insufficient long-range exchange effect. On the other hand, LC functionals accurately reproduce reaction enthalpies for these reactions. However, we noticed that even LC functionals present poor reaction enthalpies for specific reactions, in which many branches are produced or very small molecules such as methane molecule participate.

Keywords Density functional theory (DFT) · Long-range correction (LC) scheme · Condensation reaction enthalpies

1 Introduction

The field of organocatalysis has become notable current interests by chemists due to huge potential from both economical and environmental perspective. It represents not only a powerful and diverse field in synthesis but also acts as complementary to metal-catalysis and still remains an open field [1–5]. In particular, the involvement of aldol [6], Mannich [7] and α-aminoxylation [8] reactions in organocatalytic enantioselective chemistry has been proved as a testimony for synthetic utility [9]. In these reactions, C–C and C–O bond-forming transformations can play vital roles to synthesize valuable chiral compounds. Unfortunately, experimental enthalpies for these types of reactions are unavailable. Alternatively, the computational predication of such thermochemical quantities is important to pave the path in harnessing the power of these reactions in the area of synthetic applications, new organocatalytic paradigm development and enzyme catalysis design.

In previous theoretical investigations of aldol, Mannich and α-aminoxylation reactions, density functional theory (DFT) using hybrid B3LYP functional [10, 11] has been mainly used to investigate the mechanisms of stereoselectivity [12–22] and even to design novel catalysts [23–27]. Until relatively recently, the performance of this functional had not been questioned even when it had been compared to experimental values [28]. However, Check and Gilbert recently reported that B3LYP consistently underestimates reaction energies for carbon–carbon bond formations regardless of basis set used [29]. Houk et al. [28] then found that B3LYP also poorly reproduces aldol, Mannich and α-aminoxylation reaction enthalpies. They also suggested that although some up-to-date functionals perform well for aldol and Mannich reactions, even these functionals provide poor enthalpies for α-aminoxylation

---

Dedicated to Professor Shigeru Nagase on the occasion of his 65th birthday and published as part of the Nagase Festschrift Issue.

Electronic supplementary material The online version of this article (doi:10.1007/s00214-011-0944-6) contains supplementary material, which is available to authorized users.

R. K. Singh · T. Tsuneda (✉) · K. Hirao
Advanced Science Institute, RIKEN,
Wako, Saitama 351-0198, Japan
e-mail: tsuneda@riken.jp

R. K. Singh · T. Tsuneda · K. Hirao
CREST, Japan Science and Technology Agency (JST),
Tokyo 113-8656, Japan

reactions with about double errors. In contrast, the second-order Møller–Plesset perturbation theory was found to give accurate enthalpies for all these reactions. However, it has not so far been figured out why no functional consistently reproduces accurate enthalpies for all these reactions as far as we know. Since these reactions play a major role in the field of organocatalysis, it is urgent need to reveal the cause of the poor enthalpies of these reactions.

Recently, long-range-corrected (LC) DFT draws increasing attention in the field of quantum chemistry [30–40]. The LC-DFT for general functionals was developed by Tsuneda and Hirao [31] as an extension of the LC-local density approximation functional by Savin [30]. In LC-DFT [31], the two-electron operator in the exchange interaction is divided into the short- and long-range parts, and a conventional exchange functional and the Hartree–Fock exchange integral are adapted for the short- and long-range parts, respectively. The original LC-DFT contains only one parameter μ, which is unavoidable to adapt to exchange functionals used. Nevertheless, it has been found that LC-DFT has solved many severe problems confronted by conventional DFT functionals, such as the poor description of van der Waals bonds [32, 41, 42], the underestimation of hyper-polarizabilities of long-chain polyenes [43, 44] and diradicals [45], the underestimation of barrier heights [46] and recently the underestimation of orbital energies [47]. Due to its wide applicability, LC-DFT has been innovated to develop various functional: CAM-B3LYP [33], LC-ωPBE [37, 38], LCgau-BOP [35], Mori-Sanchez–Cohen–Yang [36] and ωB97 series [39, 40] functionals. It is therefore expected that LC-DFT would solve or at least provide a guiding principle for solving the poor enthalpy problem of aldol, Mannich and α-aminoxylation reactions, although LC-DFT and other LC functionals have so far never been applied to this problem.

In this study, we apply LC-DFT and three types of LC functionals to the benchmark set calculations of aldol, Mannich and α-aminoxylation reaction enthalpies, which were suggested by Houk et al. [28] to make clear why conventional DFTs have failed to reproduce accurate enthalpies for these reactions. After explaining the computational details in Sect. 2, we compare the calculated enthalpies to the complete basis set-quadratic Becke 3 (CBS-QB3) model chemistry [48, 49] values and figure out the cause of the poor reaction enthalpies in conventional DFT calculations in Sect. 3.

2 Computational details

In this study, we have tested the original LC-DFT and three types of LC functionals: LC-Becke 1988 (one parameter) exchange + one-parameter progressive correlation (LC-BOP) [31] (parameter $\mu = 0.47$ [34]; 3 parameters in total), LCgau-BOP, in which the short-range part of the two-electron operator is attenuated with a Gaussian function (parameters $\mu = 0.47$, $a = 0.0335$, and $k = -5.9$; 5 parameters in total) [35], LC-ωPBE, which is derived from the density matrix form of Perdew–Burke–Ernzerhof exchange functional (parameter $\omega = 0.4$; 1 parameter + 10 fundamental constants in total) [37, 38] and CAM-B3LYP, in which a constant rate of the Hartree–Fock exchange integral is mixed (parameters $\mu = 0.33$, $a = 0.19$ and $b = 0.46$; 12 parameters in total) [33]. To ascertain the clear cause for the large errors in conventional DFT energetics for these reactions, hybrid B3LYP (9 parameters in total) [10, 11] and hybrid meta-generalized-gradient-approximation (meta-GGA) BMK (19 parameters) [50] and M06-2x (29 parameters) [51] functionals are also examined. For each of these functionals, geometries and zero-point vibrational frequencies were computed using the aug-cc-pVTZ [52, 53] basis set. For reference, the results with cc-pVTZ and cc-pVDZ basis sets are also presented in the supporting information. As reference values, we used reaction enthalpies at zero Kelvin computed using the CBS-QB3 [48, 49] results given in Ref. [28]. All the calculations have been performed using a development version of the GAUSSIAN 09 program [54] where we have implemented LC-BOP and LCgau-BOP.

3 Results and discussion

Table 1 shows the calculated reaction enthalpies (ΔH_{0K}, kcal mol^{-1}) of the representative aldol, Mannich and α-aminoxylation reactions [28] illustrated in Fig. 1 for LC functionals (LC-BOP, LCgau-BOP, LC-ωPBE and CAM-B3LYP) and non-LC popular functionals (B3LYP, BMK and M06-2x) along with reference CBS-QB3 results. The total mean absolute errors (MAEs) from the CBS-QB3 results indicate that LC functionals give better enthalpies than those of non-LC functionals: MAEs of LC functionals (1.6–2.8 kcal mol^{-1}) are much smaller than that of B3LYP (5.0 kcal mol^{-1}) and equivalent to or even smaller than those of BMK and M06-2x with many parameters (both 2.6 kcal mol^{-1}). This result indicates that long-range exchange interactions may be one of the main reasons for the enthalpies of these reactions. To confirm the high reproducibilities of LC functionals for reaction enthalpies, we offer detailed analyses for each kind of reactions in the following paragraphs.

In aldol reactions, a C–C bond is formed of two C–H bonds with the H transfer from C to O. As shown in Table 1, the calculated results depict that the high reproducibilities of LC functionals are quite impressive in comparison with that of B3LYP and even better than those of BMK containing many semi-empirical parameters. On

Table 1 Calculated enthalpies of aldol, Mannich, α-aminoxylation and isogyric reactions in kcal/mol

Reaction	LC-BOP	LCgau-BOP	LC-ωPBE	CAM-B3LYP	B3LYP	BMK	M06-2x	CBS-QB3[a]
(1)	−16.5	−15.4	−17.3	−13.8	−9.7	−13.2	−17.4	−14.6
(2)	−10.7	−9.9	−11.7	−8.1	−3.4	−8.0	−12.6	−11.3
(3)	−16.4	−15.6	−17.4	−13.9	−9.4	−13.5	−18.2	−15.6
(4)	−5.7	−5.0	−6.6	−2.9	2.3	−2.4	−9.5	−9.2
MAE (aldol)	1.7	1.6	1.9	3.0	7.6	3.4	1.7	–
(5)	−19.1	−18.0	−20.9	−16.1	−12.0	−16.9	−18.8	−16.9
(6)	−14.3	−13.4	−16.2	−11.3	−6.7	−12.6	−15.1	−14.4
(7)	−19.3	−18.3	−21.2	−16.3	−12.0	−17.3	−19.6	−18.2
MAE (Mannich)	1.1	0.7	2.9	1.9	6.3	0.9	1.3	–
(8)	−20.2	−18.8	−19.0	−18.9	−15.2	−21.0	−21.4	−17.0
(9)	−23.6	−22.3	−22.2	−22.1	−18.2	−24.6	−24.6	−21.1
MAE (α-aminoxylation)	2.8	1.5	1.5	1.4	2.4	3.8	3.9	–
(10)	−6.9	−6.0	−8.3	−4.8	−1.7	−3.4	−7.7	−4.0
(11)	−12.2	−11.2	−14.3	−9.7	−6.3	−9.5	−11.5	−8.6
(12)	−11.5	−10.4	−11.2	−10.7	−7.8	−12.1	−12.3	−6.8
MAE (isogyric)	3.7	2.7	4.8	2.0	1.9	2.3	4.0	–
MAE (Total)	2.2	1.6	2.8	2.2	5.0	2.6	2.6	–

Mean absolute errors from CBS-QB3 values are also shown for each reaction type. The reaction numbers correspond to those in Fig. 1

[a] Wheeler et al. [28]

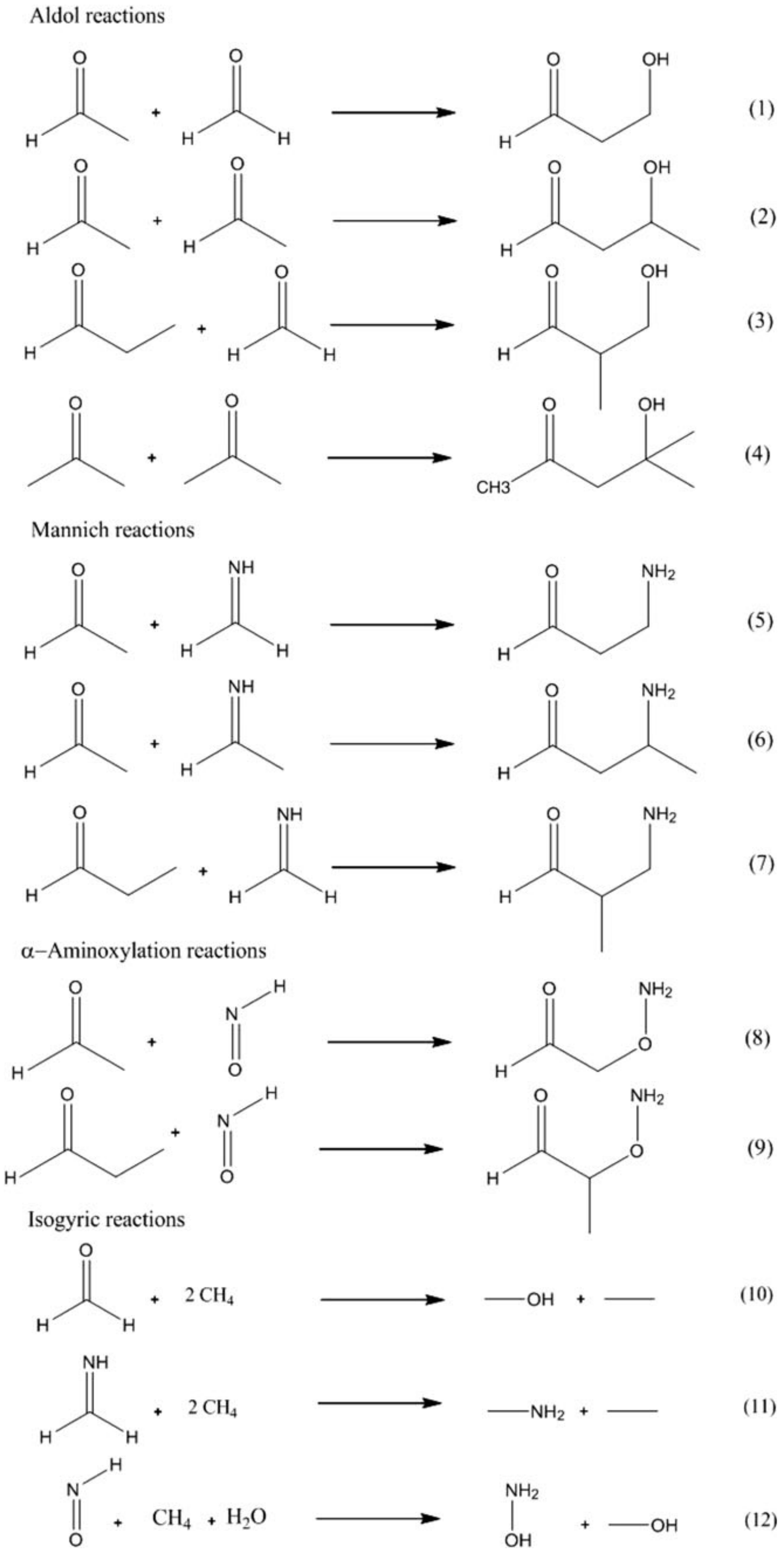
close observation, we notice that a significant error contribution comes from reaction 4. For this reaction, B3LYP gives the largest error of 11.5 kcal mol^{-1} followed by BMK (6.9 kcal mol^{-1}) and M06-2x holds minimum error of −0.3 kcal mol^{-1} while absolute error spectrum for LC functionals is between 2.6 and 6.4 kcal mol^{-1}. The main difference between reaction (4) and reactions (1)–(3) is the number of branching C–C bonds at the C atom bound with the OH group. It has been reported that such branching bonds cause large medium-range electron correlations by protobranching stabilizations [55, 56]. This indicates that the poor reaction enthalpy of reaction (4) may come from the lack of the medium-range correlations in correlation functionals besides being the lack of the long-range exchange interactions in exchange functionals of non-LC functionals.

Mannich reactions form a C–C bond of two C–H bonds with the H transfer from C to N. In Table 1, the calculated results show that the enthalpies of these reactions are well reproduced by the functionals examined in this study except for B3LYP and LC-ωPBE. We should notice that these reactions are the same reactions as aldol reactions (1)–(3) except that a C=O bond is replaced with a C=N(H) bond. That is, these reactions do not contain the Mannich reaction corresponding to reaction (4) of the aldol reactions. We, therefore, presume that the accurate reaction enthalpies of LC functionals may be due to the long-range correction similar to those of the aldol reactions. However, it is interesting to note that BMK and M06-2x also give accurate enthalpies for these reactions. We suppose that this may be attributable to the differences in the ranges of exchange interactions between the C=O and C=N(H) bonds. That is, BMK and M06-2x functionals are expected to reproduce exchange interactions in the C=N(H) bond, the range of which is supposed to be shorter than that of the C=O bond, due to the kinetic energy density terms and the constant rate of the Hartree–Fock exchange integrals in the exchange parts of these hybrid meta-GGA functionals.

For α-aminoxylation reactions, a C–O bond is formed of C–H and O=N bonds with the H transfer from C to N. Table 1 demonstrates that the long-range correction is effective to give accurate reaction enthalpies. LC functionals give much smaller MAEs than those of hybrid meta-GGA functionals. However, the performance of LC-BOP is somewhat disappointing for such reactions in comparison with the results obtained for aldol and Mannich reactions. This is obviously due to the self-interaction errors in the short-range exchange part of LC-BOP. Actually, the C–O bond may contain more short-range exchange interactions than that of the N–O bond, because the electron distribution of the C–O bond is supposed to be more localized than that of the N=O bond. This result therefore suggests that the self-interaction error in the short-range part of LC functionals should be corrected to reproduce accurate enthalpies of C–O bond formations.

To make the factors affecting these reaction enthalpies clearer, it is interesting to consider the isogyric reactions shown as reactions (10)–(12) in Fig. 1, which are

Fig. 1 Aldol, Mannich and α-aminoxylation reactions and isogyric reactions corresponding to these reactions that we calculated



fundamental reactions corresponding to aldol, Mannich and α-aminoxylation reactions, respectively. Table 1 presents the calculated enthalpies and the MAEs from the CBS-QB3 results. As a whole, LC functionals are found to give relatively large MAEs for these reaction enthalpies, while B3LYP provides accurate enthalpies in contrast to the above reaction enthalpies. We suppose that this contrasting result is due to the enthalpy of methane molecule. That is, LC functionals tend to underestimate the enthalpy of methane molecule, because the self-interaction errors in the short-range exchange interactions are essentially large in small methane molecule. In fact, electrons around the H atoms of this molecule are known to have only self-interactions [57]. In particular, LC-ωPBE gives poor enthalpies for these reactions to cause the large total MAEs. On the other hand, B3LYP gives reasonably accurate enthalpies only for these isogyric reactions. This may suggest that the high reproducibility of B3LYP is specialized to such small molecule calculations.

Finally, let us examine the decomposition of aldol, Mannich and α-aminoxylation reactions into isodesmic, homodesmotic and hyperhomodesmotic reactions for further analysis. We can write reactions (1), (5) and (8) as a sum of isogyric, isodesmic, homodesmotic and hyperhomodesmotic reactions as illustrated in Figs. 2, 3 and 4, respectively, wherein each successive reaction captures the

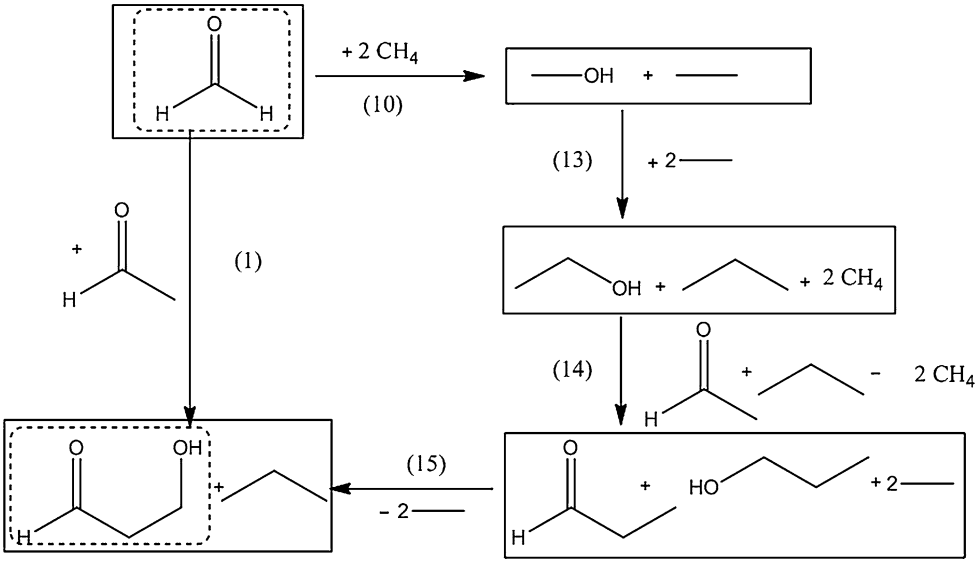


Fig. 2 Decomposition of aldol reaction (1) into a sum of isogyric (10), isodesmic (13), homodesmotic (14) and hyperhomodesmotic (15) reactions

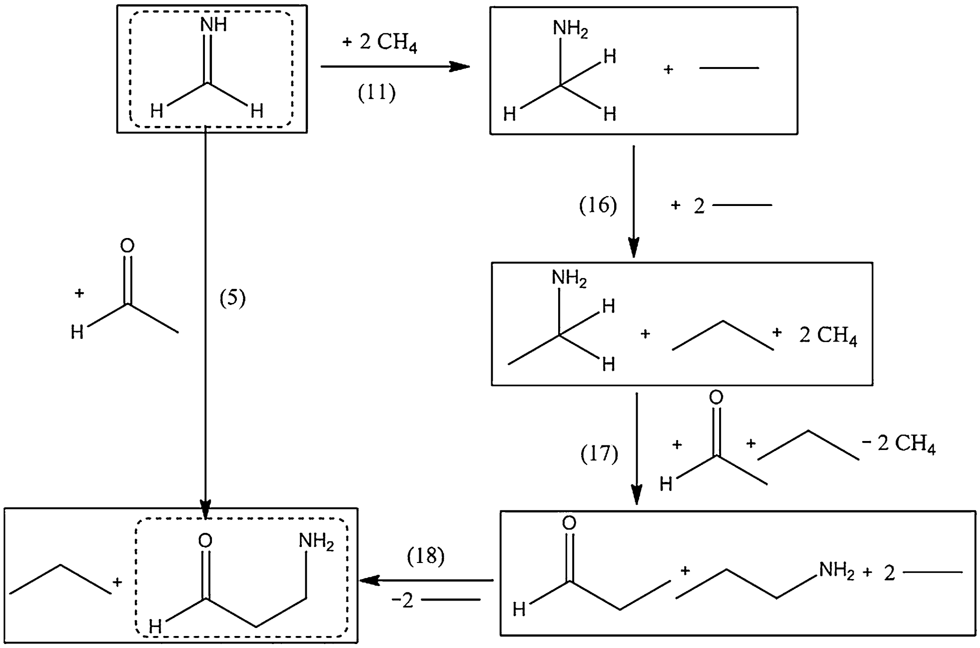


Fig. 3 Decompostion of Mannich reaction (5) into a sum of isogyric (11), isodesmic (16), homodesmotic (17) and hyperhomodesmotic (18) reactions

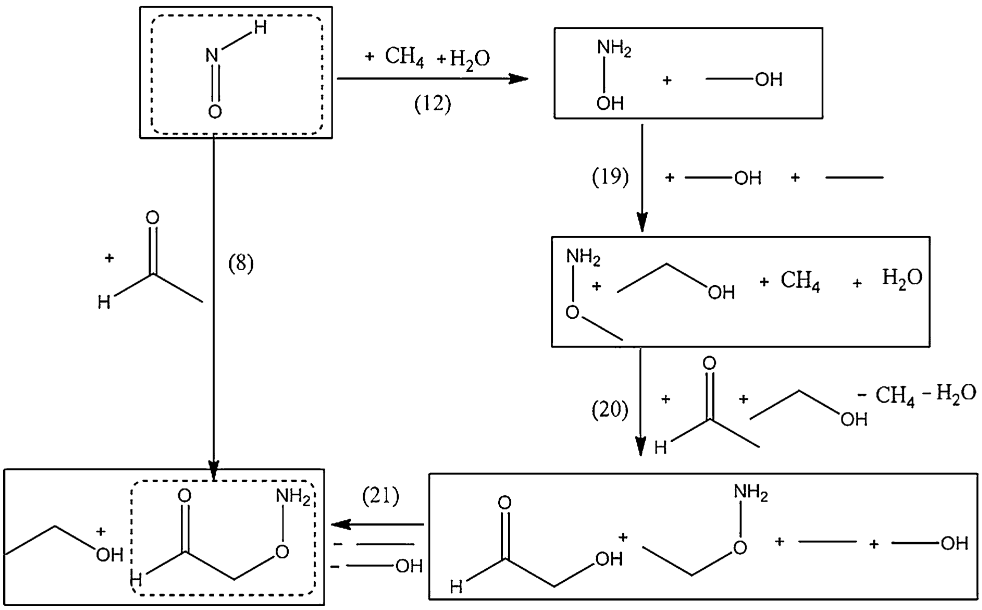


Fig. 4 Decompostion of α-aminoxylation reaction (8) into a sum of isogyric (12), isodesmic (19), homodesmotic (20) and hyperhomodesmotic (21) reactions

Table 2 Calculated reaction enthalpies of the decompositions of aldol (1), Mannich (5) and α-aminoxylation (8) reactions in kcal/mol

Reaction	LC-BOP	LCgau-BOP	LC-ωPBE	CAM-B3LYP	B3LYP	BMK	M06-2X	CBS-QB3[a]
(10)	−6.9	−6.0	−8.3	−4.9	−1.7	−3.4	−7.7	−4.0
(13)	−8.0	−8.1	−7.6	−7.8	−7.1	−9.0	−7.5	−8.8
(14)	−4.2	−4.2	−4.1	−4.0	−3.6	−2.9	−5.2	−4.7
(15)	2.6	3.0	2.7	2.8	2.8	2.1	2.9	2.9
MAE (reaction 1)	1.1	0.8	1.5	0.7	1.3	0.8	1.4	–
(11)	−12.2	−11.2	−14.3	−9.7	−6.3	−9.5	−11.5	−8.6
(16)	−6.6	−6.8	−6.3	−6.4	−5.8	−7.8	−6.3	−7.7
(17)	0.9	0.9	0.7	0.9	1.0	2.1	−0.1	0.7
(18)	−1.3	−1.0	−1.0	−1.1	−0.8	−1.8	−0.9	−1.3
MAE (reaction 5)	1.2	1.0	1.9	0.7	1.2	0.7	1.4	–
(12)	−11.5	−10.4	−11.2	−10.7	−7.8	−12.1	−12.3	−6.8
(19)	−11.1	−11.1	−10.3	−10.8	−10.2	−11.4	−11.1	−12.2
(20)	5.1	5.3	4.9	5.1	5.0	4.8	4.8	4.5
(21)	−2.6	−2.5	−2.3	−2.4	−2.1	−2.3	−2.8	−2.6
MAE (reaction 8)	1.6	1.4	1.7	1.5	1.0	1.7	1.8	–

Mean absolute errors from CBS-QB3 values are also shown for each reaction type. The reaction numbers correspond to those in Figs. 2, 3 and 4

[a] Wheeler et al. [28]

effects of long-range intramolecular effects. Table 2 shows the calculated enthalpies of the decomposition of aldol (1), Mannich (5) and α-aminoxylation (8) reactions and their MAEs with respect to CBS-QB3 results. The table indicates that all these functionals provide accurate enthalpies for these decomposed reactions. By looking at the details of the table, we found that the large errors are only given for the isogyric reactions (10), (11) and (12) mentioned above. Since the enthalpies of the aldol, Mannich and α-aminoxylation reactions are the sum of these decomposed reaction enthalpies, this result may indicate that the errors in the isogyric reaction enthalpies are cancelled out in the total reactions. To make it clear, we illustrated the relative energies for these decomposed reactions in Figs. 5, 6 and 7. The figures show that compared to CBS-QB3 results, B3LYP gives much different energy behaviours, while LC functionals give parallel energies except for the isogyric reaction ones. Interestingly, BMK and M06-2x also give different behaviours, despite these functionals give small MAEs for these decomposed reactions. As a matter of fact, we found that the signs of the errors (Table 2) are inconsistent for these functionals, in contrast

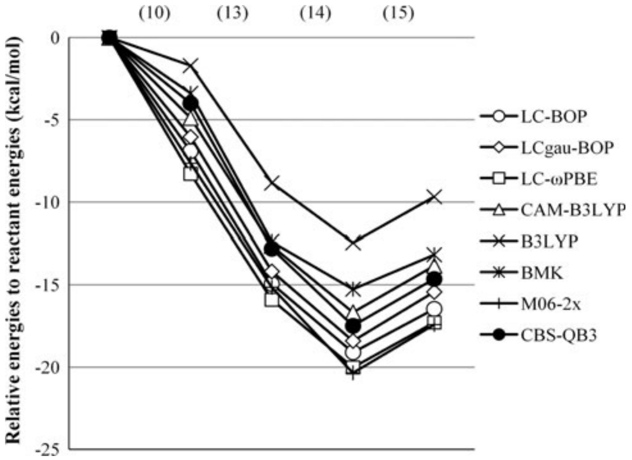


Fig. 5 Relative energies to reactant energies (kcal mol^{-1}) for the decomposition reactions of aldol reaction (1)

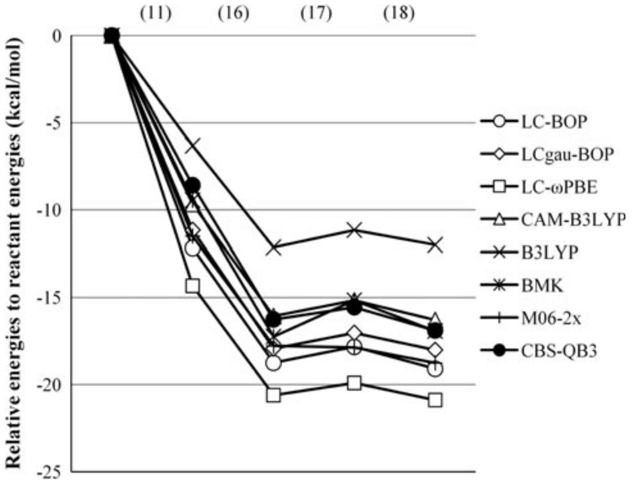


Fig. 6 Relative energies to reactant energies (kcal mol^{-1}) for the decomposition reactions of Mannich reaction (5)

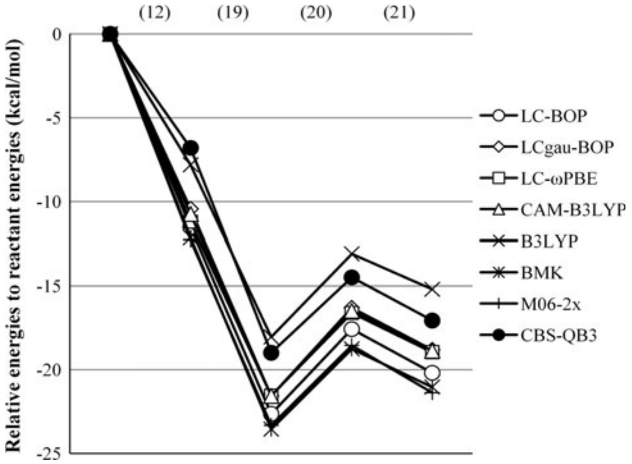


Fig. 7 Relative energies to reactant energies (kcal mol^{-1}) for the decomposition reactions of α-aminoxylation reaction (8)

to those of LC functionals. Therefore, this result strongly supports the high reproducibility of LC functionals in such promising organic reaction enthalpies calculations.

4 Conclusions

In this study, we have calculated the reaction enthalpies of aldol, Mannich and α-aminoxylation reactions by DFT with LC functionals to reveal the reason why DFT with B3LYP functional gives poor enthalpies for these reactions [28]. For these reactions, we found that LC functionals mostly give accurate reaction enthalpies with much less MAEs than B3LYP ones. This clearly indicates that B3LYP lacks long-range exchange effects to reproduce accurate enthalpies for these reactions. However, all functionals give the largest errors for a reaction producing many branches of C–C bonds, and we attribute these errors to the protobranching stabilizations due to the lack of medium-range electron correlations [55, 56]. For α-aminoxylation reactions, LC-BOP gives slightly worse enthalpies than other LC functional ones. We suggest that these errors may be due to the self-interaction errors in the short-range part of LC-BOP.

In case of isogyric reactions, B3LYP gives accurate enthalpies, while LC functionals overestimate them. We propose that the overestimations may arise from the underestimations of the enthalpy of methane molecule, for which large short-range exchange interactions may cause the severe self-interaction errors in the short-range exchange part of LC functionals. For further investigation, aldol, Mannich and α-aminoxylation reactions were decomposed into isogyric, isodesmic, homodesmotic and hyperhomodesmotic reactions, and their reaction enthalpies were computed. As a result, it is noticed that only the isogyric reactions give larger errors and are cancelled out in the total reactions. To delve this into a bit deeper, the relative enthalpies at the reaction steps were plotted and found that LC functional gives parallel energies against the reference results, except for the isogyric reactions, whereas B3LYP, BMK and M06-2x provide much different behaviours.

In summary, we conclude that long-range exchange interactions play a crucial role in aldol, Mannich and α-aminoxylation reactions, and therefore, B3LYP gives poor enthalpies for these reactions. As mentioned above, LC functionals are powerful candidates for reproducing accurate enthalpies for such organic reactions; therefore, we expect that LC functionals would give accurate reaction enthalpies and reaction barriers for a wide variety of condensation reactions, although we have not calculated them due to the lack of the reference data. However, we know that there still remain some problems even in LC calculations for specific reactions, in which many branches are produced or very small molecules such as methane molecule participate.

Acknowledgments This research was supported in part by the Core Research for Evolutional Science and Technology Program, and 'High Performance Computing for Multi-Scale and MultiPhysics Phenomena' of the Japan Science and Technology Agency (JST). We thank the RIKEN Integrated Cluster of Clusters (RICC) at RIKEN for the computer resources used for the calculation.

References

1. Dalko PI, Moisan L (2001) Angew Chem Int Ed 40:3726–3748
2. Dalko PI, Moisan L (2004) Angew Chem Int Ed 43:5138–5175
3. Pellisier H (2007) Tetrahedron 63:9267–9331
4. Melchiorre P, Marigo M, Carlone A, Bartoli G (2008) Angew Chem Int Ed 47:6138–6171
5. MacMillan DWC (2008) Nature 455:304–308
6. List B, Lerner RA, Barbas CF III (2000) J Am Chem Soc 122:2395–2396
7. List B (2000) J Am Chem Soc 122:9336–9337
8. Cordova A, Sunden H, Bogevig A, Johansson M, Himo F (2004) Chem Eur J 10:3673–3684
9. List B (2002) Tetrahedron 58:5573–5590
10. Becke AD (1993) J Chem Phys 98:5648–5652
11. Lee C, Yang W, Parr RG (1998) Phys Rev B 37:785–789
12. Bahmanyar S, Houk KN (2001) J Am Chem Soc 123:11273–11283
13. Bahmanyar S, Houk KN (2001) J Am Chem Soc 123:12911–12912
14. Rankin KR, Gauld JW, Boyd RJ (2002) J Phys Chem A 106:5155–5159
15. Bahmanyar S, Houk KN, Martin HJ, List B (2003) J Am Chem Soc 125:2475–2479
16. Clemente FR, Houk KN (2004) Angew Chem Int Ed 43:5766–5768
17. Cheong PHY, Zhang H, Thayumanavan R, Tanaka F, Houk KN, Barbas CF III (2006) Org Lett 8:811–814
18. Hayashi Y, Okano T, Itoh T, Urushima T, Ishikawa H, Uchimaru T (2008) Angew Chem Int Ed 47:9053–9058
19. Parasuk W, Parasuk V (2008) J Org Chem 73:9388–9392
20. Li H, Fu A, Shi H (2009) J Mol Catal A: Chem 303:1–8
21. Poe SL, Bogdan AR, Mason BP, Steinbacher JL, Opalka SM, McQuade DT (2009) J Org Chem 74:1574–1580
22. Diez-Martinez A, Tejero T, Merino P (2010) Tetrahedron: Asymmetry 21:2934–2943
23. Tang Z, Jiang F, Yu L-T, Cui X, Gong L-Z, Mi A-Q, Jiang Y-Z, Wu Y-D (2003) J Am Chem Soc 125:5262–5263
24. Cheong PHY, Houk KN (2005) Synthesis 9:1533–1537
25. Mitsumori S, Zhang H, Cheong PHY, Houk KN, Tanaka F, Barbas CF III (2006) J Am Chem Soc 128:1040–1041
26. Shinisha CB, Sunoj RB (2007) Org Biomol Chem 5:1287–1294
27. Houk KN, Cheong PH-Y (2008) Nature 455:309–313
28. Wheeler SE, Moran A, Pieniazek SN, Houk KN (2009) J Phys Chem A 38:10376–10384
29. Check CE, Gilbert TM (2005) J Org Chem 70:9828–9834
30. Leininger T, Stoll H, Werner H-J, Savin A (1997) Chem Phys Lett 275:151–160
31. Iikura H, Tsuneda T, Yanai T, Hirao K (2001) J Chem Phys 125:3540–3544
32. Kamiya M, Tsuneda T, Hirao K (2002) J Chem Phys 117:6010–6015
33. Yanai T, Tew DP, Handy NC (2004) Chem Phys Lett 393:51–57
34. Song JW, Hirosawa T, Tsuneda T, Hirao K (2007) J Chem Phys 126:154105-7
35. Song JW, Tokura S, Sato T, Watson MA, Hirao K (2007) J Chem Phys 127:154109-6
36. Cohen AJ, Mori-Sánchez P, Yang W (2007) J Chem Phys 126:191109-5
37. Vydrov OA, Heyd J, Krukau AV, Scuseria GE (2006) J Chem Phys 125:074106-9
38. Vydrov OA, Scuseria GE (2006) J Chem Phys 125:234109-9
39. Chai JD, Head-Gordon M (2008) J Chem Phys 128:084106-15
40. Chai JD, Head-Gordon M (2008) Phys Chem Chem Phys 10:6615–6620
41. Sato T, Tsuneda T, Hirao K (2005) J Chem Phys 123:104307-10
42. Sato T, Tsuneda T, Hirao K (2007) J Chem Phys 126:234114-11
43. Kamiya M, Sekino H, Tsuneda T, Hirao K (2005) J Chem Phys 122:234111-10
44. Sekino H, Maeda Y, Kamiya M, Hirao K (2007) J Chem Phys 126:014107-6
45. Kishi R, Bonness S, Yoneda K, Takahashi H, Nakano M, Botek E, Champagne B, Kubo T, Kamada K, Ohta K, Tsuneda T (2010) J Chem Phys 132:094107-9
46. Song JW, Watson MA, Sekino H, Hirao K (2008) J Chem Phys 129:024117-8
47. Tsuneda T, Song JW, Suzuki S, Hirao K (2010) J Chem Phys 133:174101-9
48. Montgomery JA, Frisch MJ, Ochterski JW, Petersson GA (1999) J Chem Phys 110:2822–2827
49. Montgomery JA, Frisch MJ, Ochterski JW, Petersson GA (2000) J Chem Phys 112:6532–6542
50. Boese AD, Martin JML (2004) J Chem Phys 121:3405–3416
51. Zhao Y, Truhlar DG (2008) Theor Chem Acc 120:215–241
52. Dunning JTH (1989) J Chem Phys 90:1007–1023
53. Kendall RA, Dunning JTH, Harrison RJ (1992) J Chem Phys 96:6796–6806
54. Gaussian 09, Revision **A.1**, Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA, Nakatsuji H, Caricato M, Li X, Hratchian HP, Izmaylov AF, Bloino J, Zheng G, Sonnenberg JL, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven,T, Montgomery Jr JA, Peralta JE, Ogliaro F, Bearpark M, Heyd JJ, Brothers E, Kudin KN, Staroverov VN, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant JC, Iyengar SS, Tomas J, Cossi M, Rega N, Millam NJ, Klene M, Knox JE, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts, R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Martin RL, Morokuma K, Zakrzewski VG, Voth GA, Salvador P, Dannenberg JJ, Dapprich S, Daniels AD, Farkas Ö, Foresman JB, Ortiz JV, Cioslowski J, Fox DJ (2009) Gaussian, Wallingford
55. Wodrich MD, Corminboeuf C, Schleyer PVR (2006) Org Lett 8:3631–3634
56. Wodrich MD, Wannere CS, Mo Y, Jarowski PD, Houk KN, Schleyer PVR (2007) Chem Eur J 13:7731–7744
57. Tsuneda T, Kamiya M, Hirao K (2003) J Comput Chem 24:1592–1598