Revisiting the effect of f-functions in predicting the right reaction mechanism for hypervalent iodine reagents

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Abstract
To understand the effect of f-functions in predicting the right reaction mechanism for hypervalent iodine reagents, we adopt the Ahlrichs basis set family def2-SVP and def2-TZVP to revisit the potential energy surfaces of IBX-mediated oxidation and Togni I’s isomerisation. Our results further prove that f-functions (in either Pople, Dunning, or Ahlrichs basis set series) are indispensable to predict the correct rate-determining step of hypervalent iodine reagents. The f-functions have a significant impact on the predicted reaction barriers for processes involving the I–X (X = O, OH, CF3, etc.) bond cleavage and formation, for example, in the reductive elimination step or the hypervalent twist step. We furthermore explore two hypervalent twist modes that account for the different influences of f-functions for IBX and Togni I. Our findings may be helpful for theoretical chemists to appropriately study the reaction mechanism of hypervalent iodine reagents.

1 INTRODUCTION
Hypervalent iodine reagents,1–3 such as 2-iodoxybenzoic acid (IBX) and Togni’s reagent I (Togni I) (see Scheme 1), have attracted broad interests in recent years because of their economic feasibility, eco-friendliness, and low toxicity, and both theoretical4–9 and experimental10–13 studies of these reagents have undergone an explosive growth. IBX is an important oxidant due to its ideal chemo-selectivity and mild reaction conditions.14 The IBX-mediated oxidation of alcohol mainly includes two steps, that is, (1) hypervalent twist where ligands attached to iodine are rearranged in a coordinated motion and (2) reductive elimination that involves the C–H bond cleavage. Identifying its rate-determining step (RDS) has both scientific and engineering importance. Earlier density functional theory (DFT) study15

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determined the hypervalent twist as the RDS using the MPW1K functional and the LACV3P** basis set,16 which is a combination of Pople’s 6-311G** basis set15 and the LANL2DZ effective core.17 Same conclusion has been drawn by other researchers using various functionals with basis sets similar to LACV3P**.18–21 However, this conclusion is inconsistent with the Corey’s kinetic isotope effect (KIE) experiments.22

In 2017, our theoretical study employing a wide range of basis sets at the level of both DFT and density cumulant theory (DCT) revealed that the RDS of IBX-mediated oxidation is strongly sensitive to the choice of basis sets.23 With LACV3P** as well as the Dunning basis sets without \( f \)-functions (such as cc-pVDZ(-PP) and aug-cc-pVDZ(-PP)), where the (-PP) suffix represents pseudopotential for iodine), the RDS was predicted to be the hypervalent twist step (TS1). With more complete Dunning basis sets, such as cc-pVTZ(-PP), cc-pVQZ(-PP), aug-cc-pVTZ(-PP), and aug-cc-pVQZ(-PP),24–29 all tested functionals including MPM1K,30 M06-2X,31 \( \omega \)B97X-D,32 and B3LYP33 determined the reductive elimination (TS2) as the RDS; this conclusion remains unchanged as we approach the basis set limit.23 We have attributed the two contradictory results to the effect of \( f \)-functions in the basis sets.

Another important hypervalent iodine reagent, Togni I, has been successfully applied as an oxidant to synthesize trifluoromethylated compounds in pharmaceutical and agrochemical industries.34–35 Our previous work36 has showed that Togni I can also undergo a two-step mechanism, that is, the hypervalent twist (TS3) and the reductive elimination, to form its lower-energy ether isomer. Similar to the IBX-mediated oxidation reaction, Togni I’s isomerisation was determined to feature an RDS of reductive elimination (TS4) at the B3LYP/aug-cc-pVTZ(-PP) level of theory. However, whether the \( f \)-functions play an essential role in the determination of the RDS remains to be confirmed.

In order to generalize our findings on the effect of \( f \)-functions, in the present research we adopt a different basis set family, that is, def2-SVP and def2-TZVP,37–39 to revisit the reactions of IBX-mediated oxidation and Togni I’s isomerisation. The layout of the article is as follows. In Section 2, we explain the basis sets and methods used in our work. In Section 3, we discuss the effect of \( f \)-functions on reaction mechanism of the two hypervalent iodine reagents, and further analyze the origins of such effect. In Section 4, we summarize our results.

2 | COMPUTATIONAL DETAILS

Compared to the cc-pVDZ(-PP) and cc-pVTZ(-PP) basis sets, def2-SVP and def2-TZVP have respectively similar components of contracted orbitals with a smaller number of primitive functions. The def2-SVP basis set can be described as (4s1p/2s1p) for H, (7s4p1d/3s2p1d) for C and O, and (10s7p6d/4s4p2d) for I, while the def2-TZVP basis set can be described as (5s1p/3s1p) for H, (11s6p2d1f/5s3p2d1f) for C and O, and (11s10p8d2f/6s5p3d2f) for I. Note that \( f \)-functions for C, O, and I are provided in def2-TZVP but not contained in def2-SVP. In the present work, M06-2X was chosen as the DFT functional for all computations because it has been recommended for the study of main-group thermochemistry and kinetics.31

3 | RESULTS AND DISCUSSION

3.1 | Effect of \( f \)-functions for IBX

The potential energy surface (PES) of the oxidation reaction for IBX is shown in Figure 1. Two curves (blue and green) are obtained at the M06-2X/def2-SVP and M06-2X/def2-TZVP level of theory, respectively. Additional curve (red) from M06-2X with the aug-cc-pVTZ(-PP) basis set is provided as a calibration. With the def2-SVP basis set, the hypervalent twist (TS1) as the RDS, whose energy barrier is 15.6 kcal/mol higher than that of reductive elimination (TS2). On the contrary, when the def2-TZVP basis set is adopted, the RDS is correctly predicted, with TS2 energy higher than TS1 by 8.0 kcal/mol. Figure 1 also shows that the def2-TZVP energy barriers qualitatively reproduced the aug-cc-pVTZ (-PP) results (differ by 0.1 kcal/mol for TS1 and 2.2 kcal/mol for TS2). Combining with our previous work,23 we have investigated three different basis set families, including Pople’s 6-311G**, Dunning’s correlation consistent basis sets, and Ahlrichs’ improved “def-bases”, and confirmed that the \( f \)-functions are critical to predict the correct RDS for the reactions of IBX.

3.2 | Effect of \( f \)-functions for Togni I

The isomerisation reaction path of Togni I is shown in Figure 2. With the smaller def2-SVP basis set (without \( f \)-functions, blue curve), the hypervalent twist (TS3) is predicted as the RDS, with an energy barrier 11 kcal/mol higher than that of reductive elimination (TS4). In the contrast, def2-TZVP (with \( f \)-functions, green curve) predicts the reductive elimination (TS4) as the RDS, whose energy barrier is 3 kcal/mol higher than that of TS3. Again, the PES predicted by def2-TZVP almost reproduces the aug-cc-pVTZ(-PP) results (red curve) within an energy difference of 2 kcal/mol. These results also indicate that the \( f \)-functions are critical to predict the correct RDS for the reactions of Togni I.

SCHEME 1 The structures of IBX and Togni I
3.3 | Origins of different f-function dependence

The wrong RDS predicted by def2-SVP in Figures 1 and 2 can simply be attributed to both the underestimation of the energy barrier for the reductive elimination step (TS2 or TS4) and the overestimation of the energy barrier for the hypervalent twist step (TS1 or TS3). Next, we individually analyze the two steps due to their contrasting dependence on the basis sets.

As one source of error, the underestimation of TS2 by 7 kcal/mol relative to the aug-cc-pVTZ(-PP) calibration is the main reason for the
failure of the prediction of RDS for IBX (see Figure 1). This is directly related to the more severe underestimation (by 16 kcal/mol) of the energy for the elimination product 3. In other words, the def2-SVP basis sets cannot even qualitatively predict the correct thermodynamics. As halfway through the bond-breaking process, the transition state TS2 is underestimated as well. Interestingly, the energy deviation in TS2 is about half as much as in 3. Likewise, in Figure 2, def2-SVP underestimates the reaction energy of product 6 by 14 kcal/mol compared to that predicted by aug-cc-pVTZ(-PP), and causes the related reaction barrier of TS4 to deviate from the calibration by 5 kcal/mol. Thus, the f-functions are shown to be critical to predict the correct energies for the process of the I–O (Figure 1) or I–C (Figure 2) bond breaking. In a 2011 paper by Truhlar et al., the def2-SVP basis set was used along with various DFT methods to determine the acid dissociation energy for H2AsO4, and the mean unsigned errors (MUE) was found to be 10.5 kcal/mol. However, when the def2-TZVP basis set was used, the MUE dropped off to 2.0 kcal/mol.43 This may imply that f-basis functions play important roles for these reactions involving fourth- and fifth-period main group elements.

Another source of error that leads to incorrect identification of RDS is the overestimation of energy barrier of the hypervalent twist step (TS1 in Figure 1, TS3 in Figure 2). In contrast to their significant effects on both TS2 and TS4, the f-basis functions are only important for the hypervalent twist step in Togni I reaction (TS3, Figure 2), but have less influence on that in IBX reaction (TS1, Figure 1). This difference may be explained by the different hypervalent twist pathways for the two reactions, which result in different geometries of the transition states. Our computations show that the hypervalent twist step is realized via an equatorial position in IBX but via an apical position in Togni I (Scheme 2). The equivalent terms out-of-plane and in-plane were used, respectively, in Lüthi’s work.42

As shown in Scheme 3, for the IBX reaction the hypervalent twist from 1 to the intermediate 2 is via an internal rotation around the I–Ph bond axis. In TS1, the –OCH3 and –O groups are in the equatorial positions (Scheme 3A), leaving the I–OCH3 and I–O distances almost unchanged. The endocyclic I–O bond is highly ionic, as indicated by the NBO analysis,43 and thus, in this twist mode there is no bond breaking involved, which is believed to have weak dependence on the basis sets.44 As a result, the twist energy barrier of TS1 is relatively low (<20 kcal/mol) and not significantly influenced by the f-functions.

However, for the Togni I reaction, in the hypervalent twist transition state TS3, the CF3 group is predicted to move toward the apical position (Scheme 3B). Since the CF3 group tending to the apical position must have strong interaction with the two lone pairs on the I atom (see Scheme 1), the twist step in this reaction requires higher energy (>40 kcal/mol), and the I–CF3 distance in TS3 gets lengthened by about 30%. Because the basis set overlap between I and CF3 depends on the I–CF3 distance, it is not surprising that the effect of f-basis functions is more noticeable for TS3 than for TS1.

4 | CONCLUSIONS

In summary, we adopted the Ahlrichs def2-SVP and def2-TZVP basis sets to study the two-step reactions of IBX and Togni I. Similar to our previous work with the Pople and Dunning basis set families, our present results confirm that the f-functions in Ahlrichs basis sets are important to predict the right rate-determining step (RDS).

One reason for the failure of the smaller basis sets (without f-functions) in identifying RDS is that they tend to predict significantly lower energy barriers for the I–C and I–O bond breaking (TS2 and TS4) in the reductive elimination step, compared to the results from a larger basis set (with f-functions). And such underestimation is associated with their incapability to correctly predict reaction energies.

Another reason for the prediction of wrong RDS involves the hypervalent twist step. The reaction barrier of TS1 (<20 kcal/mol) is much lower in energy than that of TS3 (>40 kcal/mol), and the effect of f-functions is different on the hypervalent twist between IBX and Togni I. This could be related to the different hypervalent twist pathways (equatorial twist pathway and apical twist pathway) and bond length changes.

Since theoretical studies for the reactions of hypervalent iodine reagents provide significant guidance for experiments, we hope our findings on the effect of f-functions could facilitate the determination of correct reaction mechanism for more hypervalent iodine reagents.
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CONFLICT OF INTEREST
There are no conflicts to declare.

DATA AVAILABILITY STATEMENT
The data that supports the findings of this study are available in the supplementary material of this article.

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