

# How Well Can New-Generation Density Functionals Describe the Energetics of Bond-Dissociation Reactions Producing Radicals?

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The performance of various density functionals has been tested for three sets of reaction energies involving radicals. It is shown that two recently designed functionals, M05-2X and M06-2X, provide the best performance. These functionals provide useful and affordable methods for future mechanistic studies involving organic radicals.

## 1. Introduction

Evidence disparaging the performance of popular density functionals for closed-shell organic systems has been presented by Curtiss et al.,<sup>1</sup> Check and Gilbert,<sup>2</sup> Carlier et al.,<sup>3</sup> Grimme et al.,<sup>4–6</sup> Schreiner et al.,<sup>7–9</sup> and Schleyer's group.<sup>10</sup> The poor performance of the most popular functional, B3LYP, is particularly discouraging because many organic chemists use it as a “black box” computational tool. Recently, we have shown that our new hybrid M05-2X<sup>11</sup> functional performs well for most of these problematic closed-shell organic systems,<sup>12–14</sup> and this good performance has been confirmed by two recent studies from other groups.<sup>15,16</sup> Subsequent work showed even better average performance by the M06-2X functional,<sup>17</sup> which can be considered to be an improved version of M05-2X.

A few recent papers also pointed out failures of popular density functionals for energetic descriptions of organic radicals.<sup>18–21</sup> Most recently, Izgorodina et al.<sup>21</sup> have tested 12 popular density functionals for calculating the enthalpies of a range of radical reactions. They found that the bond dissociation energies involving the TEMPO radical (TEMPO = 2,2,6,6-tetramethylpiperidin-1-yloxy, Figure 1) are the most problematic cases for all tested DFT functionals. For example, B3LYP gives a mean absolute deviation from benchmark values of 16 kcal/mol. Izgorodina et al.<sup>21</sup> also expressed hope that the M05-2X functional, which they were unable to include in their study, would provide an affordable yet accurate method of studying radical reactions. We have previously<sup>17</sup> tested M06-2X and M05-2X for energies of reactions involving radicals, for barrier heights of radical reactions, and for atomization energies producing radicals. In another study, the performance of M05-2X was compared to a large number of other methods for barrier heights of open- and closed-shell reactions.<sup>22</sup> In this article, we assess M05-2X and its improved successor M06-2X for the difficult cases of Izgorodina et al.'s systems<sup>21</sup> because it is important to know if M05-2X and M06-2X give the same improved performance for these open-

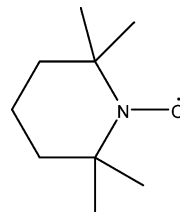


Figure 1. The TEMPO radical.

shell organic systems as that for previous tests, especially for the treatment of the kinetics<sup>23</sup> of radical reactions and  $\beta$ -scission reactions. To place the performance of new functionals in an even broader perspective, we also assess seven other promising functionals, namely, M06,<sup>17</sup> PBEh,<sup>24</sup> mPW1PW,<sup>25</sup>  $\tau$ -HCTHh,<sup>26</sup> TPSSH,<sup>27</sup> B98,<sup>28</sup> and B97-3.<sup>29</sup> Combining these results with those of Izgorodina et al.<sup>21</sup> provides a consistent systematic test of 21 density functionals on 61 thermochemical data for reactions producing radicals.

The Computational Details are described in section 2, and Results and Discussion are in section 3. Section 4 presents the Concluding Remarks.

## 2. Computational Methods

The 10 density functionals tested here have various characteristics and were selected for different reasons. M05-2X and M06-2X are hybrid meta functionals both chosen because of their excellent performance in previous tests involving organic chemistry. M06 is also a hybrid meta functional; it has broader applicability than M05-2X and M06-2X in that it also yields good results for transition-metal chemistry and other multireference cases. The  $\tau$ -HCTHh and TPSSH functionals represent, in some sense, the culminations (so far) of the extensive efforts of the Handy and Perdew groups, respectively. In contrast, mPW1PW (also called mPW1PW91, mPW0, and MPW25) and PBEh (also called PBE1PBE and PBE0) are very similar (to one another) hybrid functionals (like the popular B3LYP functional, they do not involve kinetic energy density) with a better average performance than that of B3LYP. Finally, B98 and B97-3 are the two best performing hybrid functionals,

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**TABLE 1: R–X Bond Dissociation Energies ( $D_e$ , kcal/mol) for the HBDE35 Database<sup>a</sup>**

X–R	G3(MP2)-RAD	M06-2X	M05-2X	M06	BMK	$\tau$ -HCTHh	B98	B97-3	PBEh	mPW1PW	TPSSH
H–CH <sub>3</sub>	111.9	111.8	111.8	111.8	112.5	110.6	111.2	111.7	109.3	109.0	110.9
H–CH <sub>2</sub> F	108.4	107.5	107.9	107.6	107.9	105.3	106.1	106.7	104.4	104.2	106.3
H–CH <sub>2</sub> OH	103.4	102.5	102.3	102.3	102.1	99.7	100.6	101.1	99.1	98.9	101.0
H–CH <sub>2</sub> CN	103.6	103.5	102.6	101.1	103.1	98.7	99.9	100.6	98.9	98.6	100.0
H–CH <sub>2</sub> Ph	96.5	97.0	95.6	94.3	96.2	92.6	93.7	94.3	92.9	92.6	94.3
H–CH(CH <sub>3</sub> )Ph	94.8	94.4	93.4	91.1	93.6	89.7	90.9	91.4	89.9	89.6	91.5
H–C(CH <sub>3</sub> ) <sub>2</sub> Ph	94.4	93.0	92.4	89.4	92.5	88.0	89.5	89.9	88.2	88.0	89.9
CH <sub>3</sub> –CH <sub>3</sub>	95.9	97.6	97.4	96.8	98.0	96.5	95.7	96.8	95.2	93.5	90.5
CH <sub>3</sub> –CH <sub>2</sub> F	98.4	99.1	99.5	98.5	99.1	96.8	96.3	97.3	96.1	94.5	91.4
CH <sub>3</sub> –CH <sub>2</sub> OH	92.8	93.2	92.9	92.3	92.4	90.0	89.5	90.5	89.7	88.0	84.8
CH <sub>3</sub> –CH <sub>2</sub> CN	89.6	90.8	89.9	87.3	90.1	85.8	85.6	86.8	86.0	84.3	80.7
CH <sub>3</sub> –CH <sub>2</sub> Ph	83.2	84.9	83.3	81.4	83.2	79.7	79.3	80.3	80.0	78.2	74.8
CH <sub>3</sub> –CH(CH <sub>3</sub> )Ph	82.5	82.9	81.8	78.9	81.1	76.7	76.4	77.1	77.1	75.2	71.9
CH <sub>3</sub> –C(CH <sub>3</sub> ) <sub>2</sub> Ph	82.1	81.4	80.8	77.1	79.1	73.6	73.4	73.7	74.3	72.2	68.9
CH <sub>3</sub> O–CH <sub>3</sub>	89.7	91.5	90.6	89.5	88.8	86.9	86.1	85.9	85.6	84.0	82.1
CH <sub>3</sub> O–CH <sub>2</sub> F	100.1	100.8	100.7	98.5	97.8	94.9	94.2	94.0	94.4	92.7	90.5
CH <sub>3</sub> O–CH <sub>2</sub> OH	95.6	96.0	95.3	93.5	92.1	89.2	88.5	88.2	89.0	87.4	85.2
CH <sub>3</sub> O–CH <sub>2</sub> CN	82.8	82.3	80.6	77.5	79.7	73.8	73.5	73.3	73.9	72.3	69.9
CH <sub>3</sub> O–CH <sub>2</sub> Ph	78.3	79.9	77.6	75.1	75.3	71.3	70.9	70.6	71.8	70.1	67.8
CH <sub>3</sub> O–CH(CH <sub>3</sub> )Ph	78.6	78.9	77.0	73.4	73.4	68.4	68.0	67.2	69.0	67.1	65.0
CH <sub>3</sub> O–C(CH <sub>3</sub> ) <sub>2</sub> Ph	79.6	78.8	77.2	73.4	73.5	67.6	67.3	66.5	68.3	66.5	64.2
HO–CH <sub>3</sub>	96.8	99.9	99.3	99.3	98.9	98.8	97.3	97.1	96.2	94.6	92.9
HO–CH <sub>2</sub> F	107.8	109.9	109.9	109.2	108.9	107.6	106.3	106.1	105.9	104.3	102.1
HO–CH <sub>2</sub> OH	103.7	105.5	104.9	104.6	103.7	102.5	101.2	100.8	101.0	99.4	97.3
HO–CH <sub>2</sub> CN	88.1	90.6	89.0	87.4	88.6	86.0	85.1	84.9	84.8	83.2	80.9
HO–CH <sub>2</sub> Ph	85.1	88.3	86.2	85.0	85.7	83.2	82.3	82.0	82.5	80.8	78.7
HO–CH(CH <sub>3</sub> )Ph	88.6	90.6	89.2	86.8	87.8	84.8	83.9	83.3	84.1	82.4	80.2
HO–C(CH <sub>3</sub> ) <sub>2</sub> Ph	89.5	90.4	89.4	86.5	87.5	83.6	82.8	82.0	83.1	81.3	79.0
F–CH <sub>3</sub>	114.1	115.9	116.6	117.1	116.1	117.3	115.2	114.1	112.9	111.6	112.0
F–CH <sub>2</sub> F	123.0	124.0	124.8	124.9	123.7	123.9	122.1	121.0	120.5	119.1	119.0
F–CH <sub>2</sub> OH	120.2	121.0	121.5	121.7	120.2	120.5	118.6	117.5	117.4	116.0	115.9
F–CH <sub>2</sub> CN	102.3	103.3	102.7	102.2	102.2	101.4	99.9	98.8	98.4	97.1	97.1
F–CH <sub>2</sub> Ph	102.3	104.8	104.0	103.3	103.2	102.4	100.9	99.7	99.9	98.5	98.6
F–CH(CH <sub>3</sub> )Ph	105.5	106.9	106.5	104.9	105.2	104.0	102.5	101.1	101.5	100.1	100.1
F–C(CH <sub>3</sub> ) <sub>2</sub> Ph	108.6	108.9	109.0	106.8	107.3	105.3	104.0	102.5	102.9	101.5	101.4
absolute values											
MUE <sup>b</sup>		1.2	1.1	2.1	1.5	3.8	4.0	4.1	4.3	5.7	6.8
MaxAE <sup>b</sup>		3.4	2.7	6.2	6.1	12.0	12.3	13.2	11.3	13.2	15.4
RMSE <sup>b</sup>		1.5	1.4	2.7	2.0	4.8	5.0	5.1	5.0	6.2	7.7
relative values <sup>c</sup>											
MUE		1.0	1.5	3.0	2.3	4.4	4.0	4.1	3.0	3.0	3.4
MaxAE		2.6	3.3	6.0	5.2	9.2	8.6	9.3	7.2	7.5	7.8

<sup>a</sup> All calculations were performed using B3LYP/6-31G(d)-optimized geometries. All single-point energy calculations were performed using the 6-311+G(3df,2p) basis set. The G3(MP2)-RAD and BMK results were derived from the data of Izgorodina et al.<sup>21</sup> by removing the zero-point energy, as described in section 2. <sup>b</sup> MUE = mean unsigned error = mean absolute deviation; MaxAE = maximum absolute error; RMSE = root-mean-square error. <sup>c</sup> The relative value of BDE was calculated as the difference between it and the corresponding value for R = CH<sub>3</sub>. In calculating the MUEs of the relative values, the R = CH<sub>3</sub> data were omitted as their MUEs for the relative values are equal to zero by definition.

representing the best that anybody has been able to do for main-group thermochemistry without kinetic energy density in the functional. In particular, Curtiss et al.<sup>30</sup> judged B98 to be the most accurate functional in tests against the G3/05 test set of 454 energies, and we<sup>17</sup> judged B97-3 and B98 to be the best and second-best hybrid density functional (i.e., density functionals without kinetic energy density) in tests against 350 main-group energetics (the B97-3 density functional was not included in the tests of Curtiss et al.). Table S1 of Supporting Information gives the details of all tested density functionals.

All density functional calculations were carried out using a locally modified *Gaussian 03*<sup>31,32</sup> program. The nine density functionals were tested with the B3LYP/6-31G(d) geometries and with a triple- $\zeta$  basis set, namely, 6-311+G(3df,2p).

The functionals will be tested on three databases from ref 21. The first, which will be called HBDE35, consists of 35 homolytic bond dissociation energies for R–X compounds, where  $\bullet$ R is a carbon-centered organic radical, and  $\bullet$ X is  $\bullet$ H,  $\bullet$ F,  $\bullet$ OH,  $\bullet$ CH<sub>3</sub>, or  $\bullet$ OCH<sub>3</sub>. The second, called  $\beta$ -SRE16, consists of 16 energies of the  $\beta$ -scission reactions involving RXCH<sub>2</sub> $\bullet$

$\rightarrow$  R $\bullet$  + X=CH<sub>2</sub> and RCH<sub>2</sub>(CH(Ph)) $\bullet$   $\rightarrow$  R $\bullet$  + CH<sub>2</sub>=CH(Ph) (X = CH<sub>2</sub>, O, and S; R = CH<sub>3</sub>, CH<sub>2</sub>CH<sub>3</sub>, CH(CH<sub>3</sub>)<sub>2</sub>, and C(CH<sub>3</sub>)<sub>3</sub>). The third, TBDE10, consists of 10 bond dissociation energies of TEMPO-R compounds, where R $\bullet$  is a carbon-centered organic radical. In all cases, we compute the zero-point-exclusive bond dissociation energy  $D_e$  or the zero-point-exclusive energy of reaction.

Best-available estimates are taken from ref 21; they are derived from the G3(MP2)-RAD<sup>33</sup> benchmark-quality wave function theory for the 61 cases in the HBDE35,  $\beta$ -SRE16, and TBDE10 databases. The tabulated results in the present paper are obtained by adding the spin–orbit stabilization of the product radicals to theoretically derived values (both those based on our own calculations and those based on ref 21) for the cases where it is most important, namely, dissociations producing F or OH, using values tabulated previously.<sup>34</sup> (Note: the benchmark G3(MP2)-RAD calculations of ref 21 already included this effect for reactions producing a F atom.)

In ref 21, all theoretically derived bond dissociation energies and reaction energies were adjusted to 0 K by adding the zero-

**TABLE 2: Energies of the  $\beta$ -Scission Reactions (kcal/mol),<sup>a</sup>  $RXCH_2\bullet \rightarrow R\bullet + X=CH_2$  and  $RCH_2CH(Ph)\bullet \rightarrow R\bullet + CH_2=CH(Ph)$  ( $X = CH_2, O,$  and  $S$ ;  $R = CH_3, CH_2CH_3, CH(CH_3)_2,$  and  $C(CH_3)_3$ )**

R-X	G3(MP2)-RAD	M06-2X	M05-2X	M06	BMK	$\tau$ -HCTHh	B98	B97-3	PBEh	mPW1PW	TPSSh
CH <sub>3</sub> -CH <sub>2</sub> CH <sub>2</sub> •	25.3	28.4	28.5	29.0	28.4	27.6	26.9	26.6	30.7	29.2	26.0
CH <sub>2</sub> CH <sub>3</sub> -CH <sub>2</sub> CH <sub>2</sub> •	24.4	26.5	26.5	26.1	25.9	23.9	23.4	23.0	27.5	26.1	22.7
CH(CH <sub>3</sub> ) <sub>2</sub> -CH <sub>2</sub> CH <sub>2</sub> •	23.7	25.1	25.2	24.2	23.6	20.4	19.9	19.3	24.4	22.7	19.3
C(CH <sub>3</sub> ) <sub>3</sub> -CH <sub>2</sub> CH <sub>2</sub> •	22.9	23.6	24.0	22.4	21.0	16.7	16.2	15.2	20.8	19.0	15.7
CH <sub>3</sub> -OCH <sub>2</sub> •	11.4	16.8	17.5	13.8	14.8	15.0	14.4	13.2	17.0	15.6	14.2
CH <sub>2</sub> CH <sub>3</sub> -OCH <sub>2</sub> •	13.6	17.7	18.4	13.8	15.3	14.3	14.0	12.8	17.0	15.6	14.0
CH(CH <sub>3</sub> ) <sub>2</sub> -OCH <sub>2</sub> •	14.8	18.1	18.9	13.6	15.0	13.0	12.7	11.3	16.0	14.5	12.8
C(CH <sub>3</sub> ) <sub>3</sub> -OCH <sub>2</sub> •	14.0	16.6	17.6	11.7	12.7	9.5	9.2	7.5	12.8	11.1	9.3
CH <sub>3</sub> -SCH <sub>2</sub> •	31.2	36.0	37.4	35.1	36.4	36.3	35.5	35.3	38.6	37.1	34.4
CH <sub>2</sub> CH <sub>3</sub> -SCH <sub>2</sub> •	31.3	34.9	36.3	33.1	34.7	33.3	32.7	32.3	36.2	34.6	31.8
CH(CH <sub>3</sub> ) <sub>2</sub> -SCH <sub>2</sub> •	31.0	33.5	35.2	30.9	32.7	30.2	29.7	29.1	33.5	31.8	29.0
C(CH <sub>3</sub> ) <sub>3</sub> -SCH <sub>2</sub> •	30.2	31.6	33.6	28.7	30.2	26.4	25.9	24.9	30.0	28.1	25.3
CH <sub>3</sub> -CH(Ph)CH <sub>2</sub> •	34.5	37.2	38.4	39.3	37.2	37.5	36.6	36.2	39.6	38.1	34.6
CH <sub>2</sub> CH <sub>3</sub> -CH(Ph)CH <sub>2</sub> •	34.5	35.3	36.4	36.4	35.4	33.8	33.1	32.6	36.5	34.9	31.3
CH(CH <sub>3</sub> ) <sub>2</sub> -CH(Ph)CH <sub>2</sub> •	34.0	33.4	34.8	34.1	32.7	30.1	29.5	28.6	33.2	31.4	27.9
C(CH <sub>3</sub> ) <sub>3</sub> -CH(Ph)CH <sub>2</sub> •	33.6	32.2	33.7	32.6	30.3	26.2	25.6	24.3	29.5	27.6	24.1
absolute values											
MUE <sup>b</sup>		2.5	3.3	1.7	2.0	3.1	3.2	3.6	3.1	2.8	3.3
MaxAE <sup>b</sup>		5.5	6.2	4.8	5.2	7.4	8.0	9.3	7.4	6.0	9.5
RMSE <sup>b</sup>		2.9	3.7	2.2	2.4	3.7	3.8	4.4	3.7	3.3	4.2
relative values											
MUE		2.3	2.2	3.7	3.5	6.0	5.8	6.2	5.1	5.3	5.4
MaxAE		4.2	3.9	5.8	6.0	10.4	10.1	11.0	9.2	9.6	9.6

<sup>a</sup> All calculations were performed using B3LYP/6-31G(d)-optimized geometries. All single-point energy calculations were performed using the 6-311+G(3df,2p) basis set. The G3(MP2)-RAD and BMK results were derived from the data of Izgorodina et al.<sup>21</sup> by removing zero-point energy, as described in section 2. <sup>b</sup> MUE = mean unsigned error = mean absolute deviation; MaxAE = maximum absolute error; RMSE = root-mean-square error. <sup>c</sup> The relative value of the energies of  $\beta$ -scission reactions was calculated as the difference between it and the corresponding value for  $R = CH_3$ . In calculating the MUEs of the relative values, the  $R = CH_3$  data were omitted as their MUEs for the relative values are equal to zero by definition.

point energy, thereby producing  $D_0$ . These zero-point energies were removed for the present comparisons in order to provide a purer test of density functional theory for the electronic structural component of covalent bonding affinity. The G3(MP2)-RAD  $D_0$  values from ref 21 were corrected from  $D_0$  to  $D_e$  values using zero-point energies at the B3LYP/6-31G(d) level (scaled by 0.9806).

### 3. Results and Discussion

**3.1. Validation for Prototypical Bond Homolyses.** First, we present the performance of the tested density functionals for the prototypical homolysis reactions of the HBDE35 database. Table 1 gives the R-X bond dissociation energies for  $R = CH_3, CH_2F, CH_2OH, CH_2CN,$  benzyl, 1-phenylethyl, and cumyl and  $X = H, CH_3, OCH_3, OH,$  and  $F$ . In addition to the new results for 9 density functionals, Table 1 also includes results for the BMK<sup>35</sup> functional from ref 21 because that functional had the smallest mean unsigned error of the 12 functionals in their study.

Table 1 shows that the best-performing functionals for these data are M05-2X and M06-2X, with mean unsigned errors (MUEs) of 1.1 and 1.2 kcal/mol, respectively. BMK also performs well for this database, with a MUE of 1.5 kcal/mol. These small "errors" are actually competitive with the G3(MP2)-RAD calculations and experiments in that Izgorodina<sup>21</sup> found a mean unsigned deviation of 1.5 kcal/mol between G3(MP2)-RAD and experiment for the 25 cases in the HBDE35 database for which both are available.

M06-2X and M05-2X give much smaller maximum absolute errors (MaxAEs) than other functionals. The signed deviations from G3(MP2)-RAD range from -2.4 to 2.7 kcal/mol for M05-2X and -1.4 to 3.4 for M06-2X. If we compare the relative R-X BDE, M06-2X is better than M05-2X; the MUEs are 1.0 and 1.5 kcal/mol, respectively.

**3.2.  $\beta$ -Scission Reaction Energies.** The performance for  $\beta$ -scission reaction energies is presented in Table 2. Table 2 shows that M06 give the best performance for this database, and M06-2X and M05-2X are less accurate than BMK for the absolute reaction energies. However, M05-2X and M06-2X give the best performance for the relative trends for the energies of  $\beta$ -scission reactions.

The better performance of M06 relative to M05-2X and M06-2X for this database is probably attributable to the multireference character<sup>36,37</sup> in reactions involving double bonds. M06 was designed to be valid even in cases with large multireference character,<sup>17</sup> which is often present in transition-metal chemistry.

**3.3. Performance for the Species Involving TEMPO.** Table 3 presents the results for the alkyl oxygen BDEs of nitroxides



where  $R = CH_3, CH_2CH_3, CH(CH_3)_2, C(CH_3)_3, CH_2CH_2CH_3, CH_2F, CH_2OH, CH_2CN, CH(CN)CH_3,$  and  $CH(Cl)CH_3$  and TEMPO = 2,2,6,6-tetramethylpiperidin-1-yloxy (Figure 1). Table 3 shows that M06-2X is the best performer, with a MUE of 1.8 kcal/mol and a MaxAE of 4.3 kcal/mol. M05-2X and M06 are less accurate than M06-2X for this database, but they out-perform all other popular functionals. The MUEs of PBEh,  $\tau$ -HCTHh, mPW1PW, and TPSSh are larger than 10 kcal/mol.

**3.4. Average Error.** Table 4 presents an overall assessment of 21 density functionals and 2 wave function methods, namely, RHF and RMP2, for the energetics in Tables 1, 2, and 3. The last column in Table 4 is the average mean unsigned error (AMUE), which is the average of the MUEs in Tables 1, 2, and 3. If we use AMUE to judge the performance of these functionals for energetics involving radicals, we can see that only M06-2X, M05-2X, and M06 outperform RMP2, and other functionals are less accurate. The most popular functional, B3LYP, has a large AMUE of 9.2 kcal/mol.

**TABLE 3: R–TEMPO → R• + •TEMPO Bond Dissociation Energies ( $D_e$ , kcal/mol)<sup>a</sup>**

R•	G3(MP2)-RAD	M06-2X	M05-2X	M06	BMK	$\tau$ -HCTHh	B98	B97-3	PBEh	mPW1PW	TPSSH
CH <sub>3</sub>	53.9	54.4	52.7	52.8	51.0	46.9	46.6	45.4	46.1	44.3	43.4
CH <sub>2</sub> CH <sub>3</sub>	56.6	55.3	53.6	52.8	51.4	46.0	46.0	44.6	45.9	44.1	42.9
CH(CH <sub>3</sub> ) <sub>2</sub>	55.0	52.3	50.4	49.4	47.3	40.7	40.7	38.9	41.0	38.9	37.8
C(CH <sub>3</sub> ) <sub>3</sub>	50.6	46.3	44.5	44.1	40.5	32.8	32.8	30.6	33.2	30.8	30.0
CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	56.6	55.4	53.9	53.3	51.1	46.0	46.1	44.7	46.1	44.2	42.8
CH <sub>2</sub> F	63.8	63.1	62.0	61.3	59.3	54.4	54.3	53.0	54.4	52.6	51.3
CH <sub>2</sub> OH	58.7	57.7	55.9	55.5	52.8	47.8	47.6	46.0	48.1	46.2	45.0
CH <sub>2</sub> CN	45.8	44.7	42.1	40.4	40.1	33.5	33.9	32.7	34.2	32.4	30.9
CH(CN)CH <sub>3</sub>	45.9	43.3	40.7	38.6	37.9	30.1	30.5	28.9	30.9	28.9	27.5
CH(Cl)CH <sub>3</sub>	56.3	54.0	51.9	51.9	50.0	43.3	43.5	41.4	43.1	41.1	40.5
MUE <sup>b</sup>		1.8	3.6	4.3	6.2	12.2	12.1	13.7	12.0	14.0	15.1
MaxAE <sup>b</sup>		4.3	6.1	7.2	10.1	17.8	17.8	20.0	17.4	19.8	20.6
RMSE <sup>b</sup>		2.1	3.8	4.6	6.5	12.5	12.5	14.1	12.3	14.3	15.3

<sup>a</sup> TEMPO = 2,2,6,6-tetramethylpiperidin-1-yloxy (see Figure 1); all calculations were performed using B3LYP/6-31G(d)-optimized geometries. All single-point energy calculations were performed using the 6-311+G(3df,2p) basis set. The G3(MP2)-RAD and BMK results were derived from the data of Izgorodina et al.,<sup>21</sup> as described in section 2. <sup>b</sup> MUE = mean unsigned error = mean absolute deviation; MaxAE = maximum absolute error; RMSE = root-mean-square error.

**TABLE 4: Average Errors (kcal/mol)**

method	type <sup>a</sup>	HBDE35		$\beta$ SRE16		TBDE10		AMUE <sup>b</sup>
		MaxAE	MUE	MaxAE	MUE	MaxAE	MUE	
M06-2X	HM	3.4	1.2	5.5	2.5	4.3	1.8	1.8
M05-2X	HM	2.7	1.1	6.2	3.3	6.1	3.6	2.7
M06	HM	6.2	2.1	4.8	1.7	7.2	4.3	2.7
RMP2 <sup>c</sup>	WFT	9.8	5.5	4.2	2.2	2.3	1.9	3.2
BMK <sup>c</sup>	HM	6.1	1.5	5.2	2.0	10.1	6.2	3.2
MPWB1K <sup>c</sup>	HM	7.9	2.3	7.1	2.9	12.1	7.6	4.3
MPW1B95 <sup>c</sup>	HM	8.3	2.2	6.2	2.7	13.1	8.4	4.4
BB1K <sup>c</sup>	HM	9.5	3.1	6.0	2.6	14.3	9.4	5.0
B1B95 <sup>c</sup>	HM	10.3	2.9	7.3	2.9	15.8	10.6	5.5
B3P86 <sup>c</sup>	H	10.7	2.8	6.1	2.8	17.0	11.7	5.8
$\tau$ -HCTHh	HM	12.0	3.8	7.4	3.1	17.8	12.2	6.4
B98	H	12.3	4.0	8.0	3.2	17.8	12.1	6.4
PBEh	H	11.3	4.3	7.4	3.1	17.4	12.0	6.5
PBE <sup>c</sup>	GGA	12.0	4.1	7.1	3.1	18.2	12.9	6.7
B97-3	H	13.2	4.1	9.3	3.6	20.0	13.7	7.2
mPW1PW <sup>c</sup>	H	13.2	5.7	6.0	2.8	19.8	14.0	7.5
MPW1K <sup>c</sup>	H	13.3	6.9	7.2	3.1	18.7	13.2	7.7
mPWPW <sup>c,d</sup>	GGA	14.3	4.9	9.7	3.7	21.3	15.3	8.0
TPSSH	HM	15.4	6.8	9.5	3.3	20.6	15.1	8.4
B3LYP	H	15.7	6.6	12.2	5.0	21.8	16.0	9.2
KMLYP <sup>c</sup>	H	5.7	2.0	11.5	6.7	24.9	20.2	9.7
BLYP	GGA	19.4	7.9	16.7	8.3	25.5	19.3	11.8
RHF <sup>c</sup>	WFT	37.4	26.4	18.0	8.7	30.4	22.9	19.3

<sup>a</sup> GGA: generalized gradient approximation; H: hybrid = GGA + Hartree–Fock Exchange; HM: hybrid meta = H + kinetic energy density; WFT: wave function theory. <sup>b</sup> AMUE is an average of the MUEs for HBDE35,  $\beta$ SRE16, and TBDE10. <sup>c</sup> The results for these methods were derived from the data of Izgorodina et al.<sup>21</sup> <sup>d</sup> Also called mPWPW91.

#### 4. Concluding Remarks

In the present study, we tested 9 density functionals against 3 databases of Izgorodina et al.<sup>21</sup> involving radicals. The results are merged with theirs to provide an assessment of 23 methods (21 density functionals and 2 wave function methods) for 61 bond breaking energies that produce radicals. We found that M06-2X and M05-2X have much improved performance for energetics involving radicals, and M06-2X even gives excellent performance for the alkyl oxygen BDEs of nitroxides (R–TEMPO).

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**Supporting Information Available:** Density functionals considered and ball and stick figure of TEMPO. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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