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Performance of the RB3-LYP, RMP2, and UCCSD(T) Procedures in Calculating Radical Stabilization Energies for •NHX Radicals

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N−H bond dissociation energies (BDEs) and radical stabilization energies (RSEs) associated with the •$NHCF_3$, •NHCHO, •$NHCOCH_3$, and •$NHCONH_2$ radicals have been calculated at a number of theoretical levels. These include UHF, RHF, UB3-LYP, RB3-LYP, UMP2, RMP2, UCCSD(T), and URCCSD(T) with a variety of basis sets, as well as the high-level composite methods W1, CBS-QB3, and G3X(MP2)-RAD. For these systems, particular care must be taken to ensure convergence to the lowest-energy solution of the self-consistent-field (SCF) equations. We have assessed the performance of the various levels of theory in calculating the BDEs and RSEs of the •NHX radicals and find that, although there are somewhat larger errors for the simpler methods, the performance generally parallels that observed previously for •CH_2X radicals. In particular (and in contrast to a recent report), RB3-LYP and UCCSD(T) consistently produce very good RSEs for •NHX radicals, provided that the lowest-energy solutions are correctly identified. The RMP2 RSEs, while not as good as those for •CH_2X radicals, do not show the previously claimed large errors.

1. Introduction

The effect of a substituent on the stability of a radical relative to its effect in the parent closed-shell molecule is of widespread chemical importance and is often referred to as the radical stabilization energy, or RSE.[1,2] For substituted methyl radicals, •CH_2X, the RSE is generally measured by the energy change in the isodesmic reaction:

$$\bullet CH_2X + CH_4 \rightarrow \bullet CH_3 + CH_3X \qquad (1)$$

This is equivalent to the difference in the bond dissociation energies of CH_4 and CH_3X:

$$RSE(\bullet CH_2X) = BDE(CH_4) - BDE(CH_3X) \qquad (2)$$

In recent studies,[2,3] we have carried out extensive examinations of the RSEs of substituted methyl radicals at a number of levels of theory. We find that good results are generally obtained with high-level methods such as CBS-QB3 and G3X(MP2)-RAD but that caution needs to be exercised at lower theoretical levels, where there is often incomplete cancellation of errors in reaction 1. In particular, unrestricted Møller−Plesset theory (e.g., UMP2) can lead to poor results when there is severe spin contamination in the •CH_2X radical. However, *restricted* Møller−Plesset theory (specifically RMP2) is found to be much more reliable.[2,3]

In a subsequent investigation, Song, Cheng, Fu, Liu, and Guo (SCFLG)[4] carried out an interesting study of the corresponding radical stabilization energies of substituted amino radicals, •NHX, measured as the energy change in the isodesmic reaction:

$$\bullet NHX + NH_3 \rightarrow \bullet NH_2 + NH_2X \qquad (3)$$

This is equivalent to the difference in bond dissociation energies between NH_3 and NH_2X:

$$RSE(\bullet NHX) = BDE(NH_3) - BDE(NH_2X) \qquad (4)$$

SCFLG[4] found good results with the G3 and CBS-Q methods and also agreed with our finding that methods such as UMP2 could produce poor results in the cases of radicals showing high spin contamination. However, they also concluded that RMP2 is unreliable in several cases, specifically •$NHCF_3$, •$NHCOCH_3$, and •$NHCONH_2$. They also found that RB3-LYP performs poorly for •$NHCF_3$. In addition, they concluded that even UCCSD(T) fails for the •NHCHO radical. Although it is entirely possible that methods such as RMP2 and UCCSD(T) may have greater difficulty in describing •NHX radicals than •CH_2X radicals, we felt that it was a sufficiently important question to warrant additional scrutiny.

In the present paper, we reexamine the performance of selected levels of theory in calculating BDEs and RSEs for these designated amino radicals, i.e., •NHX with X = CF_3, CHO, $COCH_3$, and $CONH_2$. We find that there are multiple solutions of the self-consistent-field (SCF) equations in these cases and that care must be taken in order to achieve the lowest-energy solution. When this is done, the very large errors found by SCFLG[4] for RB3-LYP, RMP2, and UCCSD(T) no longer occur.

2. Theoretical Procedures

Standard ab initio molecular orbital theory[5] and density functional theory[6] calculations were carried out with the GAUSSIAN 98[7] and MOLPRO 2002.3[8] computer programs. Calculations on radicals were performed either with a restricted-open-shell reference wave function, designated with an ‘R’ prefix (e.g., RHF, RMP2), or with an unrestricted-open-shell wave function, designated with a ‘U’ prefix (e.g., UHF, UMP2). The frozen-core (fc) approximation was employed in all MP2 and CCSD(T) calculations. To facilitate comparisons with the

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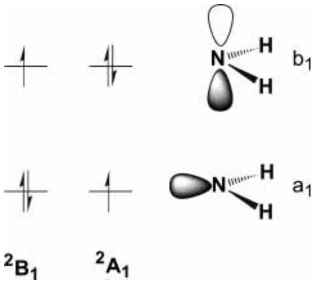

Figure 1. Occupation of orbitals in the ground ($^2B_1$) and first excited ($^2A_1$) states of the $\bullet NH_2$ radical.

TABLE 1: Energy Differences between the $^2A''$ or Pseudo-$^2A''$ Ground State and the $^2A'$ Excited State of $\bullet$NHX Radicals (0 K, kJ mol^{-1})[a]

X	UHF	RHF	CBS-QB3	G3X(MP2)-RAD	W1	expt[b]
H	139.2	136.3	132.7	135.3	131.6	133.1
CF_3	127.8[c]	125.1[c]	121.8	124.0[c]		
CHO	52.1	31.7	26.0[c]	28.9[c]	22.8[c]	
$COCH_3$	45.1	27.1	18.2[c]	14.9[c]		
$CONH_2$	71.2[c]	69.9[c]	89.2[c]	86.3[c]		

[a] See text for details. [b] See ref 15. [c] Note that for these radicals the C_s $^2A'$ structure is a saddle point on the potential energy surface at the theoretical levels specified. See text.

results of SCFLG,[4] bond dissociation energies (BDEs) and radical stabilization energies (RSEs) were obtained from geometries optimized at the UB3-LYP/6-31+G(d) level followed by single-point energy calculations with the 6-31+G(d) basis set at the following theoretical levels: UHF, RHF, UB3-LYP, RB3-LYP, UMP2, RMP2, UCCSD(T), and URCCSD(T). Unscaled UB3-LYP/6-31+G(d) zero-point vibrational energies were used in these calculations, again to facilitate comparisons with the earlier work. Additional BDEs and RSEs were obtained through single-point calculations at all these theoretical levels with the 6-311+G(2df,p) basis set on UB3-LYP/6-31G(d) optimized geometries, incorporating UB3-LYP/6-31G(d) zero-point vibrational energies scaled by a factor of 0.9806.[9] Finally, high-level results were obtained with CBS-QB3[10,11] and G3X(MP2)-RAD,[12] and with W1,[13] the latter providing the ultimate benchmarks unless otherwise noted. In recent studies,[14] we have suggested that the spin-correction term of CBS-QB3[10,11] may be somewhat overestimated in certain cases. We therefore report here results with and without the spin correction, the latter being denoted U-CBS-QB3 to distinguish it from the standard CBS-QB3 procedure. Details of the theoretical procedures may be found in the original publications[10-13] or in our recent $\bullet CH_2X$ study.[2]

3. Results and Discussion

A. States of the Amino and Substituted Amino Radicals. The $\bullet NH_2$ radical has two low-lying states that may be classified according to whether the unpaired electron is in a b_1 orbital ($^2B_1$ state in C_{2v} symmetry, equivalent to $^2A''$ in C_s symmetry) or in an a_1 orbital ($^2A_1$ state in C_{2v} symmetry, equivalent to $^2A'$ in C_s symmetry) (see Figure 1). It is well established that the ground state of $\bullet NH_2$ is $^2B_1$, with the $^2A_1$ state lying approximately 133 kJ mol^{-1} higher in energy.[15]

In examining substituted amino radicals, $\bullet$NHX, it is important to bear in mind that substituents may affect this ordering of states and that distortions from C_s symmetry will allow mixing of $^2A'$ and $^2A''$. Geometries of the $\bullet$NHX radicals were initially obtained at the UB3-LYP/6-31+G(d) level in C_s symmetry, for both $^2A''$ and $^2A'$ states. Where such C_s structures were indicated through frequency calculations to represent saddle points on the surface, reoptimizations in C_1 symmetry were performed. The global minimum was found in all cases to correspond either to a $^2A''$ state of C_s symmetry or to a pseudo-$^2A''$ state of C_1 symmetry.

Calculated energy differences between the ground-state structure, either $^2A''$ or pseudo-$^2A''$, and the lowest energy $^2A'$ state are presented in Table 1. The C_s $^2A'$ structures are found in several cases to be saddle points on the potential energy surface, and so their relative energies represent an energy gap to constrained structures. Distortions from such structures lead monotonically downhill to the pseudo-A'' minima. For the purpose of comparison with the results of SCFLG,[4] we have also carried out single-point calculations on C_1 structures with an A'-like wave function. These results are referred to as pseudo-A', but they do not have real physical significance.

Although it is not a primary emphasis in the current study, we note that the calculated $^2B_1 - {}^2A_1$ splittings between the states for the parent $\bullet NH_2$ system are in good agreement with the experimental value (133.1 kJ mol^{-1})[15] at all the levels of theory presented (Table 1). There is also good agreement between the HF and high-level values for the $^2A' - {}^2A''$ splittings for the $\bullet NHCF_3$ radical. However, for the carbonyl-substituted radicals, the results change significantly in moving from HF to the high-level procedures, although it is reassuring that the latter agree well with one another. The splitting between the states varies greatly with substitution. Table 1 shows that the range is about 15−135 kJ mol^{-1}. The CHO and $COCH_3$ substituents provide significant relative stabilization to the $^2A_1$ state through delocalization of the nitrogen lone pair into the π* orbital of the carbonyl, thus substantially lowering the $^2A' - {}^2A''$ splitting.

B. Bond Dissociation Energies (BDEs). Table 2 presents a comparison of the N−H BDEs obtained by SCFLG[4] at the UHF, RHF, UB3-LYP, RB3-LYP, UMP2, RMP2, and UCCSD(T) levels (all with the 6-31+G(d) basis set), with values obtained at these levels in the present study. Table 3 presents results obtained with these theoretical procedures and the 6-311+G(2df,p) basis set. Also included in Table 3 are N−H BDEs obtained with the high-level W1 procedure of Martin et al.,[13] which are used as a benchmark, as well as with the high-level CBS-QB3 and G3X(MP2)-RAD procedures.

Comparison with the Results of SCFLG.[4] Examination of the BDEs in Table 2 shows differences from the previously reported results of SCFLG[4] by up to 200 kJ mol^{-1}. For $\bullet NHCF_3$, the differences observed with RHF, RB3-LYP, and RMP2 between the present results and those of SCFLG[4] are in the range 175−200 kJ mol^{-1}. For $\bullet$NHCHO, there are differences of 50−120 kJ mol^{-1} at the UHF, UMP2, and UCCSD(T) levels. For $\bullet NHCOCH_3$, differences of 80−110 kJ mol^{-1} are observed with RHF and RMP2. Finally, for $\bullet NHCONH_2$, differences of 70−180 kJ mol^{-1} are observed at the RHF and RMP2 levels.

What is responsible for the huge differences between the BDEs obtained in the study of SCFLG[4] and in the present study? SCFLG[4] attributed their discrepant results in these cases to poor performance by the theoretical procedures. However, we do not agree with this assessment. Rather, we have been able to trace the problem to convergence to the wrong SCF solution in each of the anomalous cases in the study by SCFLG.[4] Essentially, the incorrect solutions correspond to an A' state (for $\bullet NHCF_3$) or to a pseudo-A' state (for $\bullet$NHCHO, $\bullet NHCOCH_3$, and $\bullet NHCONH_2$). By appropriately manipulating the wave function, we are able to reproduce such results.[16]

Assessment of Results. It is convenient to use the high-level W1 benchmark results listed in Table 3 to assess the perfor-

TABLE 2: N−H Bond Dissociation Energies Associated with •NHX Radicals (0 K, kJ mol^{-1})[a,b]

X	UHF	RHF	UB3-LYP	RB3-LYP	UMP2	RMP2	UCCSD(T)	URCCSD(T)
H								
previous work[c]	301.7	313.4	426.3	430.1	401.2	401.2	392.0	
present study	301.9	313.3	426.1	430.2	401.3	401.2	392.2	392.3
CF_3								
previous work[c]	316.7	525.1	433.0	615.9	418.0	607.9	406.7	
present study	314.2	328.6	433.2	437.3	417.9	417.4	406.7	406.7
CHO								
previous work[c]	443.9	370.3	452.3	461.1	537.2	442.7	485.3	
present study	328.2	370.1	452.0	461.1	480.1	442.7	421.8	421.1
$COCH_3$								
previous work[c]	331.4	466.5	441.4	448.9	460.7	516.3	413.8	
present study	331.4	359.4	441.5	449.1	461.0	434.2	414.0	416.5
$CONH_2$								
previous work[c]	322.6	515.9	423.4	429.3	417.6	484.1	400.4	
present study	322.4	337.3	423.6	429.2	417.7	415.6	400.5	400.4
MAD[d]	139.0	116.9	23.3	17.2	25.3	36.4	51.6	51.2
LD[e]	−146.1	−130.9	−28.0	−22.4	−42.9	−43.0	−53.6	−53.2

[a] Corresponding to the energy change for the reaction $NH_2X \rightarrow$ •NHX + •H. [b] Obtained from single-point calculations with the 6-31+G(d) basis set on the UB3-LYP/6-31+G(d) geometries. [c] From SCFLG.[4] [d] Mean absolute deviation from benchmark values (W1 unless otherwise specified). [e] Largest deviation from benchmark values (W1 unless otherwise specified).

TABLE 3: N−H Bond Dissociation Energies Associated with •NHX Radicals at Higher Theoretical Levels (0 K, kJ mol^{-1})[a]

X	UB3-LYP[b]	RB3-LYP[b]	UMP2[b]	RMP2[b]	UCCSD(T)[b]	URCCSD(T)[b]	G3X(MP2)-RAD	CBS-QB3[c]	W1
H	431.5	436.3	433.1	432.0	425.0	425.1	439.7	444.2 (444.4)	444.2
CF_3	438.4	443.8	447.1	445.6	436.9	437.0	451.0	455.8 (456.0)	455.3
CHO	460.7	470.6	514.3	476.0	457.1	455.9	467.6	470.2 (475.2)	474.3
$COCH_3$	449.3	457.6	496.5	468.7	450.4	449.3	463.1	463.4 (466.8)	*d*
$CONH_2$	431.3	436.9	449.9	446.4	433.0	432.8	447.8	449.6 (450.4)	451.6
MAD	16.4	9.6	18.0	6.0	18.1	18.6	4.8	2.2 (0.8)	0.0
LD	−20.3	−14.7	+40.0	−12.2	−19.2	−19.1	−6.7	−4.2 (−1.2)	0.0

[a] Corresponding to the energy change for the reaction $NH_2X \rightarrow$ •NHX + •H. [b] Obtained from single-point calculations with the 6-311+G(2df,p) basis set on the UB3-LYP/6-31G(d) geometries. [c] Values in parentheses obtained without the spin-correction term (U-CBS-QB3). [d] Benchmark value taken as 467.6 kJ mol^{-1}; see text.

mance of simpler levels of theory for the calculation of the BDEs associated with the •NHX radicals.

•*NH_2*. Of the high-level methods, W1 and CBS-QB3 perform best, and both give an N−H BDE for NH_3 of 444.2 kJ mol^{-1}, compared with the experimental BDE of 446.6 ± 1.3 kJ mol^{-1}.[15] G3X(MP2)-RAD yields a BDE of 439.7 kJ mol^{-1}. The results obtained with the direct methods listed in Table 2 in conjunction with the 6-31+G(d) basis set are in poorer agreement with experiment. At the extreme is UHF/6-31+G(d), which gives a BDE for NH_3 that is more than 140 kJ mol^{-1} less than the W1 benchmark value. The use of restricted wave functions with the 6-31+G(d) basis set gives little improvement over the unrestricted equivalents. RB3-LYP/6-31+G(d) gives the best result with the smaller basis set. Increasing the size of the basis set to 6-311+G(2df,p) leads to a noticeable improvement for all methods, and they all yield BDEs for NH_3 that are within 20 kJ mol^{-1} of the W1 value.

•*$NHCF_3$*. The benchmark W1 BDE for NH_2CF_3 to give the $^2A''$ ground state of the •$NHCF_3$ radical is 455.3 kJ mol^{-1}. The CBS-QB3 and G3X(MP2)-RAD BDEs agree well with the benchmark, giving values of 455.8 and 451.0 kJ mol^{-1}, respectively. The direct methods when used with the 6-31+G(d) basis set do not perform as well, but there is again considerable improvement in all cases on going to the larger 6-311+G(2df,p) basis set.

•*NHCHO*. The W1 procedure gives an N−H BDE for NH_2CHO of 474.3 kJ mol^{-1}. The CBS-QB3 and G3X(MP2)-RAD levels again agree well with the benchmark value, giving N−H BDEs of 470.2 and 467.6 kJ mol^{-1}, respectively. Even closer agreement with W1 is obtained when the spin-correction term in CBS-QB3 is omitted (U-CBS-QB3), giving 475.2 kJ mol^{-1}. Of the direct methods, UMP2 fortuitously performs the best with the 6-31+G(d) basis set, giving a BDE of 480.1 kJ mol^{-1}. However, the UMP2 result actually worsens on going from 6-31+G(d) to 6-311+G(2df,p), in contrast to the behavior with the other theoretical procedures, where the improvement in basis set is accompanied by an improvement in the calculated BDEs.

•*$NHCOCH_3$*. Due to the size of this species, it was not possible to calculate the N−H BDE at the W1 level with our existing computing resources. To provide a suitably reliable BDE, we have used the G3X(MP2)-RAD RSE of −23.4 kJ mol^{-1} (see below) in conjunction with the W1 BDE of 444.2 kJ mol^{-1} for •NH_2 to obtain a benchmark BDE of 467.6 kJ mol^{-1}. The CBS-QB3 and G3X(MP2)-RAD BDEs for •$NHCOCH_3$ of 463.4 and 463.1 kJ mol^{-1}, respectively, are slightly less than this benchmark value, as is also observed for •NHCHO. Again, the CBS-QB3 result is improved (to 466.8 kJ mol^{-1}) when the spin-correction term is omitted (U-CBS-QB3). We can see from Table 2 that UMP2/6-31+G(d) again fortuitously gives the closest agreement with the benchmark, a result that becomes worse with the larger 6-311+G(2df,p) basis set. The other theoretical procedures all give improved BDEs with the 6-311+G(2df,p) basis set.

•*$NHCONH_2$*. The three composite methods all agree well for the N−H BDE of NH_2CONH_2. The benchmark W1 value is 451.6 kJ mol^{-1}, while the CBS-QB3 and G3X(MP2)-RAD procedures give BDEs of 449.6 and 447.8 kJ mol^{-1}, respectively. U-CBS-QB3 gives 450.4 kJ mol^{-1}. There is improvement on going from 6-31+G(d) to 6-311+G(2df,p) with all the direct methods.

TABLE 4: Radical Stabilization Energies of •NHX Radicals (0 K, kJ mol^{-1})[a,b]

X	UHF	RHF	UB3-LYP	RB3-LYP	UMP2	RMP2	UCCSD(T)	URCCSD(T)
CF_3								
previous work[c]	−14.6	−211.7	−7.1	−185.4	−16.7	−206.7	−14.6	
present study	−12.3	−15.3	−7.0	−7.1	−16.6	−16.2	−14.5	−14.5
CHO								
previous work[c]	−142.2	−56.9	−25.9	−31.0	−136.0	−41.4	−93.3	
present study	−26.3	−56.8	−25.9	−30.9	−76.8	−41.4	−29.6	−28.8
$COCH_3$								
previous work[c]	−29.7	−153.1	−15.1	−18.8	−59.4	−115.1	−24.3	
present study	−29.5	−46.1	−15.3	−18.9	−59.7	−33.0	−21.8	−24.3
$CONH_2$								
previous work[c]	−20.5	−202.5	2.5	0.8	−16.3	−82.8	−8.4	
present study	−20.5	−24.0	2.5	1.0	−16.5	−14.3	−8.3	−8.1
MAD	6.1	17.5	6.6	4.4	24.4	8.2	1.6	1.6
LD	−13.1	−26.6	+9.9	+8.4	−46.6	−11.2	−3.4	−3.4

[a] Corresponding to the energy change for the reaction •NHX + NH_3 → •NH_2 + NH_2X. [b] Obtained from single-point calculations with the 6-31+G(d) basis set on the UB3-LYP/6-31+G(d) geometries. [c] From SCFLG.[4]

TABLE 5: Radical Stabilization Energies of •NHX Radicals at Higher Theoretical Levels (0 K, kJ mol^{-1})[a]

X	UB3-LYP[b]	RB3-LYP[b]	UMP2[b]	RMP2[b]	UCCSD(T)[b]	URCCSD(T)[b]	G3X(MP2)-RAD	CBS-QB3[c]	W1
CF_3	−6.9	−7.5	−14.0	−13.6	−11.9	−11.9	−11.3	−11.6 (−11.6)	−11.1
CHO	−29.2	−34.4	−81.2	−44.0	−32.1	−30.8	−27.9	−26.0 (−30.8)	−30.2
$COCH_3$	−17.8	−21.4	−63.4	−36.7	−25.4	−24.3	−23.4	−19.1 (−22.4)	*d*
$CONH_2$	0.2	−0.7	−16.8	−14.4	−8.0	−7.7	−8.2	−5.4 (−6.0)	−7.4
MAD	4.6	4.1	25.8	9.2	1.3	0.7	0.8	2.8 (0.9)	0.0
LD	+7.6	+6.7	−51.0	−13.8	−2.0	−0.9	+2.3	+4.3 (+1.4)	0.0

[a] Corresponding to the energy change for the reaction •NHX + NH_3 → •NH_2 + NH_2X. [b] Obtained from single-point calculations with the 6-311+G(2df,p) basis set on the UB3-LYP/6-31G(d) geometries. [c] Values in parentheses obtained without the spin-correction term (U-CBS-QB3). [d] Benchmark value taken as −23.4 kJ mol^{-1}, see text.

General Comparisons. Tables 2 and 3 include mean absolute deviations (MADs) and largest deviations (LDs) from benchmark values (W1 unless otherwise specified) for the five BDEs. Although the sample set is too small to be statistically significant, some useful general features do emerge. We note to begin that the T_1 diagnostic values[17] calculated at the UCCSD/AVTZ//UB3-LYP/cc-pVTZ level of theory are 0.013, 0.034, 0.031, and 0.026 for •$NHCF_3$, •NHCHO, •$NHCOCH_3$, and •$NHCONH_2$, respectively. This suggests that •NHCHO, •$NHCOCH_3$, and •$NHCONH_2$ in particular represent challenging targets for calculations based on a single-reference configuration. In a related vein, the $\langle S^2 \rangle$ values found at UMP2/6-31+G(d)//UB3-LYP/6-31+G(d) for •$NHCF_3$, •NHCHO, •$NHCOCH_3$, and •$NHCONH_2$ are 0.759, 0.959, 0.907, and 0.783, respectively. This suggests potential difficulties for UMP with •NHCHO and •$NHCOCH_3$, as is indeed observed.

We find that the composite W1, CBS-QB3, and G3X(MP2)-RAD methods give results that agree well with one another and with the only experimental BDE for the •NHX radicals. CBS-QB3 without the spin-correction term (U-CBS-QB3) performs particularly well, with an MAD from W1 of just 0.8 kJ mol^{-1} and an LD of −1.2 kJ mol^{-1}. Of the simpler levels of theory, RB3-LYP performs best with the 6-31+G(d) basis set, giving an MAD of 17.2 kJ mol^{-1}. When the larger 6-311+G(2df,p) basis set is used, RB3-LYP and RMP2 produce the best results, with MADs of 9.6 and 6.0 kJ mol^{-1}, respectively. We emphasize that care must be taken to converge to the lowest-energy SCF solutions to avoid spuriously anomalous results.

C. Radical Stabilization Energies (RSEs). The radical stabilization energy of a substituted amino radical •NHX provides a measure of the effect of the substituent X on the stability of the •NHX radical relative to its effect in the parent closed-shell molecule NH_2X. It is given by the energy change in reaction 3 (above). Equivalently, it represents the difference in BDEs of NH_3 and NH_2X.

Table 4 presents a comparison of the RSEs for •NHX radicals obtained by SCFLG[4] at the UHF, RHF, UB3-LYP, RB3-LYP, UMP2, RMP2, and UCCSD(T) levels (all with the 6-31+G(d) basis set) with values obtained at these levels in the present study. Table 5 presents results obtained with these theoretical procedures and the 6-311+G(2df,p) basis set. Also included in Table 5 are the RSEs obtained with the high-level W1 procedure of Martin et al.,[13] which are used as a benchmark unless otherwise noted, as well as with the high-level CBS-QB3 and G3X(MP2)-RAD procedures.

Comparison with the Results of SCFLG.[4] Examination of the RSEs in Table 4 shows differences from the previously reported results of SCFLG[4] of up to 200 kJ mol^{-1}. These are not unexpected, given the discrepancies in the N−H BDEs discussed above. However, the calculated RSEs in Tables 4 and 5 make it clear that it is the SCFLG[4] values that are anomalous. For example, for •$NHCF_3$, all the RSEs determined in the present study lie within 6 kJ mol^{-1} of the W1 benchmark (Table 5). In contrast, the RHF, RB3-LYP, and RMP2 values of SCFLG[4] differ by 170−200 kJ mol^{-1} from the W1 value. Likewise, anomalous RSEs from the previous work of SCFLG[4] can be seen for •NHCHO at the UHF, UMP2, and UCCSD(T) levels, for •$NHCOCH_3$ with RHF and RMP2, and for •$NHCONH_2$ with RHF and RMP2. The anomalous results all have their origins in convergence to the wrong SCF solution in the previous study, and not to poor performance of the theoretical procedures as had been previously concluded.[4]

Assessment of Results. As with the BDEs discussed in the previous section, the RSEs determined with the high-level W1 procedure generally represent the benchmark values for this study and are presented in Table 5. For •$NHCOCH_3$, for which we do not have a W1 RSE, we have taken the G3X(MP2)-RAD value as the benchmark. The benchmark RSEs are thus −11.1 (•$NHCF_3$), −30.2 (•NHCHO), −23.4 (•$NHCOCH_3$), and −7.4 (•$NHCONH_2$) kJ mol^{-1}, respectively.

It can be seen from Tables 4 and 5 that for many of the theoretical procedures there is substantial cancellation of errors in the calculated RSEs; that is, the MADs are significantly smaller than corresponding MADs for BDEs (Tables 2 and 3). This is not unexpected, given the nature of the equation defining the radical stabilization energies (eq 3). The basis set dependence of the RSEs is much smaller than for the BDEs; that is, the RSEs determined with the 6-31+G(d) basis set are not substantially inferior to those obtained with the 6-311+G(2df,p) basis. The worst results (indicating less complete cancellation of errors) are observed with RHF and UMP2. This can be ascribed in the latter case to variable spin contamination in the reactant and product radicals of eq 3.

Both G3X(MP2)-RAD and CBS-QB3 give RSEs that compare well with the W1 benchmark values. The MADs and LDs are 0.8 and +2.3 kJ mol^{-1}, respectively, for G3X(MP2)-RAD and 2.8 and +4.3 kJ mol^{-1}, respectively, for CBS-QB3. For U-CBS-QB3, the MAD and LD from W1 decrease to just 0.9 and +1.4 kJ mol^{-1}, respectively.

Of the direct methods, best results are obtained with URCCSD(T)/6-311+G(2df,p). The MAD is just 1.2 kJ mol^{-1}, while the LD is 3.0 kJ mol^{-1}. Although URCCSD(T)/6-311+G(2df,p) provides a direct means of obtaining accurate RSEs, it is computationally intensive and would not be tractable for systems of moderate to large size. A more economical though still reliable procedure would be desirable.

In our previous studies on •CH$_2$X radicals,[2,3] we found RMP2/6-311+G(2df,p)//UB3-LYP/6-31G(d) to provide a cost-effective means of obtaining reasonable RSEs. The results of the present study suggest that although it is also a reasonable possibility for •NHX radicals, the discrepancies from benchmark values are somewhat larger. The MAD for RMP2/6-311+G(2df,p)//UB3-LYP/6-31G(d) is 9.2 kJ mol^{-1} with an LD of −13.8 kJ mol^{-1}. The MAD and LD for RMP2/6-31+G(d)//UB3-LYP/6-31+G(d) are 8.2 and −11.2 kJ mol^{-1}, respectively, which are slightly better than the RMP2/6-311+G(2df,p)//UB3-LYP/6-31G(d) results. We do not believe these differences to be statistically significant.

The UMP2/6-31+G(d) and UMP2/6-311+G(2df,p) RSEs show large deviations from the benchmark values for •NHCHO and •NHCOCH$_3$. This supports the conclusion that UMP2 has difficulty with species that show large spin contamination. As noted above, the $\langle S^2 \rangle$ values found at UMP2/6-31+G(d)//UB3-LYP/6-31+G(d) for •NHCHO and •NHCOCH$_3$ are 0.959 and 0.907, respectively.

Both UB3-LYP and RB3-LYP show relatively small MADs and LDs for their calculated RSEs. With the 6-31+G(d) basis set, the MADs and LDs are 6.6 and +9.9 kJ mol^{-1}, respectively, for UB3-LYP, and 4.4 and +8.4 kJ mol^{-1}, respectively, for RB3-LYP. With the 6-311+G(2df,p) basis set, the MADs and LDs are slightly better at 4.6 and +7.6 kJ mol^{-1}, respectively, for UB3-LYP and 4.1 and +6.7 kJ mol^{-1}, respectively, for RB3-LYP. One shortcoming of UB3-LYP/6-31+G(d), RB3-LYP/6-31+G(d), and UB3-LYP/6-311+G(2df,p) is that they predict positive RSEs for •NHCONH$_2$ (i.e., a relative stabilizing effect in the radical), in contrast to the small negative benchmark value.

UHF/6-31+G(d) provides good RSEs for three of the •NHX radicals when compared with the benchmark values. The largest deviation at this level is −13.1 kJ mol^{-1} for •NHCONH$_2$. While RMP2 performs significantly better than UMP2, changing from an unrestricted to a restricted approach at the HF level actually leads to a deterioration in the results. Thus with the 6-31+G(d) basis set, the MADs and LDs are 6.1 and −13.1 kJ mol^{-1}, respectively, for UHF and 17.5 and −26.6 kJ mol^{-1}, respectively, for RHF. With the 6-311+G(2df,p) basis set,[18] the MADs and LDs are slightly worse at 7.0 and −14.3 kJ mol^{-1}, respectively, for UHF and 19.8 and −30.8 kJ mol^{-1}, respectively, for RHF.

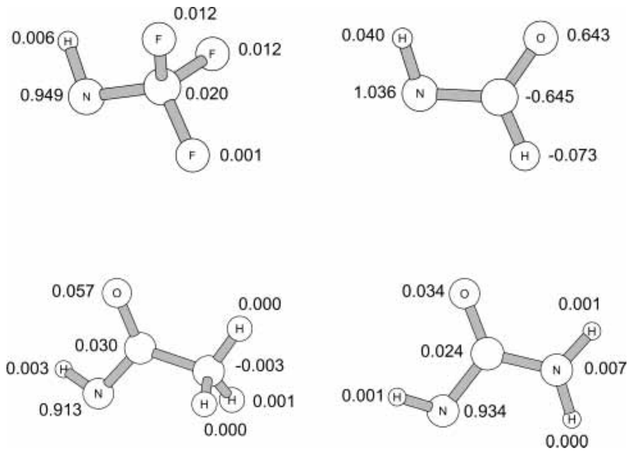

Figure 2. RMP2/6-31+G(d)//UB3-LYP/6-31+G(d) spin distributions for the •NHCF$_3$, •NHCOCH$_3$, and •NHCONH$_2$ radicals, and UCCSD(T)/6-31+G(d)//UB3-LYP/6-31+G(d) spin distribution for the •NHCHO radical.

In summary, there is good agreement among the high levels of theory (W1, G3X(MP2)-RAD, and CBS-QB3) in the calculation of RSEs. U-CBS-QB3 gives results that are particularly close to W1. UCCSD(T) and URCCSD(T) also perform very well. RB3-LYP is the best of the computationally less demanding procedures. RMP2 performs somewhat less well for •NHX radicals than found previously for •CH$_2$X radicals, although the results are still reasonable. Very poor results found previously[4] with RB3-LYP, RMP2, and UCCSD(T) may be attributed to convergence to the wrong SCF solutions. UMP2 sometimes gives large errors for RSEs and therefore should not be used when spin contamination is significant. RHF can also produce poor RSEs.

Substituent Effects in •NHX Radicals. The calculated radical stabilization energies in Tables 4 and 5 are all negative. This means that the •NHX radicals are destabilized relative to the corresponding closed-shell molecules NH$_2$X in each case. This effect is discussed in detail by SCFLG, based on G3 and CBS-Q results.[4] In brief, the negative RSEs can be rationalized in terms of a reduction in the delocalization of the nitrogen lone pair that can take place in NH$_2$CHO, NH$_2$COCH$_3$, and NH$_2$CONH$_2$, when moving to the •NHX radicals. This reduction arises because the electronic ground state is now pseudo-^{2}A″, and so it is the unpaired electron rather than the lone pair that is more strongly delocalized. The negative RSE for •NHCF$_3$ may be attributed largely to the electron-withdrawing nature of the CF$_3$ substituent destabilizing the electron-deficient radical center.

D. Spin Distributions. The discrepancies found in the BDEs and RSEs for the •NHCF$_3$, •NHCOCH$_3$, and •NHCONH$_2$ radicals at RMP2/6-31+G(d) were attributed by SCFLG[4] to a failure of RMP2 to correctly assign the spin distribution. They pointed out that for these three radicals RMP2 predicts an oxygen-centered radical, whereas the unpaired electron is mainly localized on the nitrogen with UB3-LYP and UCCSD(T). We find from the present study that the calculations of SCFLG[4] in these cases correspond to the excited ^{2}A′ state for •NHCF$_3$ and to pseudo-^{2}A′ states for •NHCOCH$_3$ and •NHCONH$_2$. For the A′ and pseudo-A′ states, the unpaired electron is indeed centered on the oxygen. On the other hand, we find that if the correct ground-state A″ or pseudo-A″ state is examined, the spin is localized on nitrogen in all cases. Figure 2 displays the RMP2/6-31+G(d) spin distributions for the ^{2}A″ ground state of

•NHCF$_3$ and the pseudo-^{2}A″ ground states of •NHCOCH$_3$ and •NHCONH$_2$. It is clear that the unpaired electron is localized on the nitrogen in all three radicals, in agreement with UB3-LYP and UCCSD(T).

Similarly, SCFLG[4] found that their UCCSD(T) calculation incorrectly assigns the unpaired electron in •NHCHO largely to the oxygen, in contrast to UB3-LYP and RMP2, which assign the electron to the nitrogen. In this case also the result may be attributed to their convergence to the higher-energy pseudo-^{2}A′ state. Figure 2 includes the spin distribution for the pseudo-^{2}A″ ground state of •NHCHO at UCCSD(T)/6-31+G(d). Again it is clear that if the correct ground state is examined, the unpaired electron is mainly localized on nitrogen.

4. Concluding Remarks

A primary purpose of the present study has been to reexamine the conclusion reached by SCFLG[4] that for several •NHX radicals, specifically •NHCF$_3$, •NHCHO, •NHCOCH$_3$, and •NHCONH$_2$, RHF, RMP2 RB3-LYP, and UCCSD(T) can lead to unrealistic spin localization and hence to poor BDEs and RSEs. They state that their results "justify many people's suspicion that the use of the spin-restricted wave function method is not always safe". This assessment is not correct. We find that the poor performance is associated with calculations being performed on excited A′ states or unphysical pseudo-A′ solutions to the SCF equations for the •NHX radicals. Once the correct ground state is used in the BDE and RSE calculations, the very large errors observed previously disappear.

The high-level W1, G3X(MP2)-RAD, and CBS-QB3 procedures all yield RSEs that agree closely with one another. CBS-QB3 performs particularly well when the spin-correction term is omitted (U-CBS-QB3). We find with the direct theoretical procedures that the difference between using 6-31+G(d) and 6-311+G(2df,p) basis sets in the calculation of RSEs is relatively small. UCCSD(T) and URCCSD(T) give very good RSEs, while RB3-LYP provides a very cost-effective alternative. The performance of RMP2 is reasonable though not as good as found previously for •CH$_2$X radicals.

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Supporting Information Available: Table S1 contains calculated total energies for the ground states (A″ or pseudo-A″) of •NHX radicals calculated at various levels of theory with the 6-31+G(d) basis set on UB3-LYP/6-31+G(d) optimized geometries. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) For an extensive list of references, see ref 2.

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(16) Note that the incorrect energies in Table 2 correspond to A′ or pseudo-A′ calculations carried out at the particular level on B3-LYP/6-31+G(d) structures that have been optimized for the A″ or pseudo-A″ state. They are therefore significantly higher than the energies that would be derived from the splittings in Table 1, in which the A′ calculations have been carried out on optimized A′ structures.

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(18) The individual UHF/6-311+G(2df,p)/UB3-LYP/6-31G(d) (RHF/6-311+G(2df,p)/UB3-LYP/6-31G(d) values in parentheses) BDEs (in kJ mol^{-1}) are as follows: NH$_3$ 306.8 (319.7), NH$_2$CF$_3$ 321.6, (334.9) NH$_2$CHO 336.2, (380.6) NH$_2$COCH$_3$ 339.3 (369.4), NH$_2$CONH$_2$ 328.5 (344.9). The corresponding RSEs are as follows: •NHCF$_3$ −14.8 (−15.3), •NHCHO −29.4 (−61.0), •NHCOCH$_3$ −32.5 (−49.8), •NHCONH$_2$ −21.7 (−25.2).