

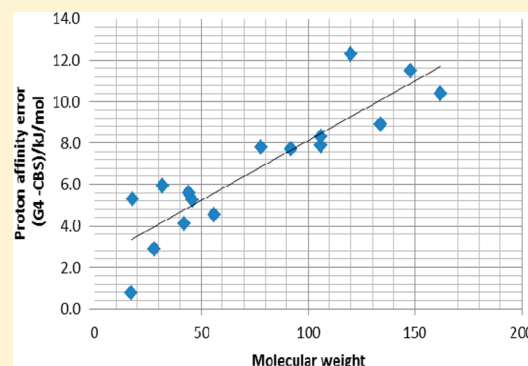
Proton Affinity Calculations with High Level Methods

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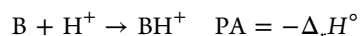
S Supporting Information

ABSTRACT: Proton affinities, stretching from small reference compounds, up to the methylbenzenes and naphthalene and anthracene, have been calculated with high accuracy computational methods, viz. W1BD, G4, G3B3, CBS-QB3, and M06-2X. Computed and the currently accepted reference proton affinities are generally in excellent accord, but there are deviations. The literature value for propene appears to be 6–7 kJ/mol too high. Reported proton affinities for the methylbenzenes seem 4–5 kJ/mol too high. G4 and G3 computations generally give results in good accord with the high level W1BD. Proton affinity values computed with the CBS-QB3 scheme are too low, and the error increases with increasing molecule size, reaching nearly 10 kJ/mol for the xylenes. The functional M06-2X fails markedly for some of the small reference compounds, in particular, for CO and ketene, but calculates methylbenzene proton affinities with high accuracy.



INTRODUCTION

When chemical reactions where protonation/deprotonation take place are to be investigated knowledge of the proton affinities (PA) of the species involved is important. A large amount of work has been expended over several decades to measure and estimate proton affinities for a considerable number of compounds. An extensive collection of generally accepted proton affinities are given in the NIST WebBook database.¹ They are the result of a critical evaluation of available experimental and, to some extent, theoretical data on PAs in the literature. A recent overview on PAs with emphasis on theoretical works has been given by Maksić et al.² The PA of a compound B is defined by the enthalpy change of the gas phase reaction



Experimental methods for PA determination are based on various mass spectrometry techniques. Relative PAs are obtained with quite good accuracy, but obtaining absolute values has been more difficult.

With the advent of steadily more powerful computers allowing increasingly more accurate molecular energy calculations quite a few papers on computed absolute PAs have appeared, but computations with highly accurate methods are still scarce. Fairly recently Czako et al. published very accurate computational results for the PAs of CO and NH₃. They found PA(CO) = 592.4 ± 0.2 kJ/mol and PA(NH₃) = 852.6 ± 0.3 kJ/mol.³ Accurate PAs are therefore now available both at the very low end and at the very high end of the PA scale, and these results may serve as needed anchoring points for relative experimental measurements. Corresponding, or nearly corresponding, high accuracy absolute values are not available in the

PA midrange where a large number of important organic compound PAs are found.

During a theoretical study of reactions taking place in protonated alkylbenzenes we found it of interest to calculate the alkylbenzene PAs. Because of some systematic discrepancies between the NIST WebBook values and the results obtained by the composite computational methods Gaussian-3 (G3B3)⁴ and the “complete basis set method” (CBS-QB3)⁵ and also a systematic deviation between results obtained with these two methods it was found worthwhile to investigate the issue more thoroughly.

COMPUTATIONAL

The computations have been carried out using the Gaussian 09 program package.⁶ The computational work was carried out at the Oslo University computer ABEL (Megware computers.)

Because CBS-QB3 and G3B3 gave clearly deviating results it was found necessary to extend the number of computational schemes. Computations have therefore also been carried out with Gaussian-4 (G4) and Weizmann-1 (W1, W1BD).^{7,8} They are both more accurate than G3 and CBS, but they are also much more demanding on computational resources—in particular, the W1 computations. The Density Functional Theory (DFT) method M06-2X is much less demanding than G3 and CBS and is claimed to be fairly accurate.⁹ Computations with this functional may be extended to larger systems where the W1 and Gn (i.e., G₁, G₂, G₃, G₄) methods as well as CBS are prohibitively time-consuming. M06-2X was therefore, somewhat arbitrarily, chosen for additional calcu-

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Table 1. Proton Affinities (kJ mol⁻¹) Calculated with Various Calculation Schemes and the Values Given by the NIST Collection

	NIST	W1BD	G4	G3B3	G2 ^a	CBS ^b	M062X ^c
Small Molecules							
NH ₃	853.6	853.8	855.1	855.7	853.6	854.3	851.3
water	691.0	690.3	691.4	689.3	688.4	686.1	697.6
CO	594.0	592.9	594.6	596.0	593.0	591.7	575.4
ethylene	680.5	681.2	680.9	678.5	681.9	677.2	681.8
formaldehyde	712.9	712.6	712.5	712.1	711.8	708.5	711.9
methanol	754.3	754.5	755.3	754.3	754.3	749.4	754.7
propene	751.6	745.0	744.5	743.2	744.3	740.4	750.3
ketene	825.3	821.6	825.1	823.8	825.0	820.1	805.2
CO ₂	540.5	539.9	541.9	540.2	539.3	536.3	535.6
acetaldehyde	768.5	770.7	769.9	769.2	770.2	765.3	772.8
ethanol	776.4	777.3	777.5	776.4		772.2	777.8
DME ^d	792.0	791.3	792.0	792.4	792.0	784.8	787.0
acetone	812.0	815.7	814.7	814.7	811.9	810.2	818.9
isobutene	802.1	803.1	802.1	801.2	802.1	797.5	809.8
Medium Molecules							
benzene	750.4	746.7	746.4	746.7		738.6	741.8
toluene	784.0	779.9	781.0	781.9		773.3	779.2
o-xylene	796.0	793.9	792.4	793.3		784.5	792.9
m-xylene	812.2	807.0	807.4	808.2		799.5	807.2
p-xylene	794.4	790.0	788.8	789.2	790.0	780.3	781.0
123TMB ^e			815.8	816.6			814.3
124TMB			817.6	818.4			815.2
135TMB	836.2		830.9	831.0		818.6	832.3
1235TEMB ^f	845.6		839.3	839.4		830.8	841.2
1245TEMB			820.0	820.0		811.1	817.2
PMB ^g	850.7		847.9	844.7		835.8	846.8
HMB ^h	860.6		861.2	861.1		850.8	859.9
naphthalene	802.9		801.3	801.9		795.5	798.3
anthracene	877.3		868.7	869.4		861.9	868.8

^aTaken from ref 11. ^bCBS-QB3. ^cBasis set cc-PVTZ. ^dDimethyl ether. ^eTrimethylbenzene. ^fTetramethylbenzene. ^gPentamethylbenzene. ^hHexamethylbenzene.

lations of a fair number of PAs, thus allowing an evaluation of the accuracy of this rather recent DFT functional.

RESULTS AND DISCUSSION

There are very few computational studies of PAs where high accuracy computational methods like G4 and W1 (W1BD) have been utilized. It was therefore found worthwhile to also include some well-known molecules which also serve as anchoring points for the PA scale, i.e. carbon monoxide CO, ammonia NH₃, water H₂O, carbon dioxide CO₂, methanol CH₃OH, ethanol C₂H₅OH, dimethyl ether CH₃OCH₃, acetone CH₃-CO-CH₃, ethene CH₂=CH₂ and propene CH₃-CH=CH₂, acetaldehyde, formaldehyde, and ketene. The absolute PAs of these compounds, *M*, are largely based on ionization threshold measurements. They may allow determination of enthalpies of formation of the MH⁺ ions when enthalpies of formation of relevant neutral species are known.^{1,10} Theoretical computations, notably by the Gaussian-2 (G2) method have also been important.¹¹ Relative PA values, typically obtained by studying equilibria in proton transfer reactions of the type A + HB⁺ → AH⁺ + B, can then be given an absolute significance. These PA values are essentially the ones given in the NIST WebBook. With today's high end PCs and workstations, computations on molecules with only two or three non-hydrogen atoms are carried out in minutes or some hours.

The molecules that are treated in this paper are given in Table 1. Proton affinities have been computed by several methods, W1BD, G4, G3B3, CBS-QB3, and M06-2X. In addition G2 values, almost all from ref 11 are given for most small molecules. The absence of W1 computations on the larger methylbenzenes will be noticed. W1 computations are very demanding when applied on molecules that are not really small, and the effort increases roughly with *N*⁷ (*N* = number of basis functions), so it was not considered worthwhile to go beyond the xylenes. The computation on protonated *p*-xylene (C₁ symmetry) took more than 200 h using 16 processors and 50 GB of memory, and already a trimethylbenzene might easily require two to three times as long.

The table which gives the species in the same order as the molecular weights is divided in two parts. The part comprising small molecules, from ammonia to isobutene, is discussed first.

The Small Molecules. The calculations of the PAs of CO and NH₃ by the investigated computational methods are considered particularly important because the PAs of these compounds are known with very high accuracy from the work of Czako et al.³ CO and NH₃ therefore serve as checkpoints for the various calculation methods that are used. Only methods that agree closely with Czako et al. can be considered to be possibly generally trustworthy. As might be expected there is an excellent agreement between the PA values according to the W1BD scheme and the "exact" PA values given by Czako et al.

for CO and NH₃. They found PA(CO) = 592.4 ± 0.3 kJ/mol and PA(NH₃) = 852.6 ± 0.3 kJ/mol. It is also to be noted that the PA values for CO and NH₃ given by the NIST WebBook are in quite satisfactory agreement with the “exact” values reported by Czako et al. It is also observed that the composite methods G4, G3B3, G2, and CBS-QB3 are in acceptable accord with Czako et al., but G3B3 overestimates the carbon monoxide and ammonia PAs with 3.6 and 3.1 kJ/mol.

Turning now to a comparison between PA values in the NIST WebBook and the values obtained with W1BD, G4, G3B3, and G2; a generally good agreement is seen. It is also clear that PAs calculated with the CBS composite method are typically 4–5 kJ/mol lower than NIST WebBook values and the values obtained with the other composite methods. The PA values computed with the M06-2X functional show no particular trend, but they fluctuate strongly when compared with NIST PAs and computed results from the composite methods. PA values calculated with this functional can therefore not be considered to be very accurate. It may, however, be worth noting that the, by far, largest deviations are found in CO and ketene (H₂C=C=O). When protonated, these molecules have the atomic arrangements H–CO and H₃C–CO. The CO bond lengths of these species are calculated to be very short and the CO bonds might formally be considered being triple bonds. Such unusual bonds may be outside the capability of the M06-2X functional.

Although computed and NIST WebBook results are generally in good accord, propene and acetone exhibit deviations. The NIST propene PA value appears to be about 7 kJ/mol too high compared with W1BD and the other composite methods, and the acetone PA seems slightly low, about 3 kJ/mol below the values from W1, and the Gn methods. Ketene raises a different issue. The Gn results and the NIST WebBook value agree very well, but the W1BD computation gives in this case a PA value which is 2 to 3.5 kJ/mol lower. The trustworthiness of the theoretical computations is therefore not fully clear. However, Bouchoux et al.¹³ published a reassessment of the PA of ketene at about the same time as Hunter and Lias¹⁰ published their comprehensive tables that are the basis for the NIST WebBook. The ketene PA found by Bouchoux et al. is 822.6 ± 3.4 kJ/mol. The difference between this value and the NIST value is within the probable uncertainty, but the reassessment by Bouchoux et al. suggests that the PA obtained at the W1BD level is more accurate than the Gn results, as one would expect because of the much higher level of theory involved in the W1BD computations.

Isobutene is one of the reference standards in the comprehensive compilation of Hunter and Lias¹⁰ and the NIST WebBook. Its absolute PA value has been uncertain, and it was adjusted downward from a much higher value, to 802.1 kJ/mol by Hunter and Lias in their 1998 compilation. This value which is retained in the NIST WebBook is partly based on Smith and Radom's work¹² where the PA was calculated using the G2 composite method.⁵ As seen from Table 1 the PA 802.1 kJ/mol is in excellent accord with the other Gn methods and W1BD. Later East and Radom pointed out that determination of the PA of isobutene is a difficult issue.¹⁴ It is not clear that the results from the Gn and W1 schemes can be utilized directly because hindered rotations of the methyl groups are neglected. In isobutene there are two methyl groups that behave as two essentially independent hindered rotors with barriers of approximately 9 kJ/mol (from B3LYP/6-31G(d)

computations). When isobutene is protonated to a *tert*-butyl cation a new methyl group is created. If, in this case, a calculation where one methyl group is rotated in steps of 5.0 degrees with full equilibration for each step (Gaussian keyword opt(modredundant)) is carried out, a barrier about 0.5 kJ/mol is found, corresponding to an essentially free rotation. However, during this rotation the other two methyl groups experience quite important torsions (partial rotations), showing that there is considerable interaction between the methyl groups. If, in such a calculation, the orientation of one of the other methyl groups is kept fixed, the barrier increases to about 4.5 kJ/mol, which is still much below the barrier in nonprotonated isobutene, but in no way a free rotation. The third methyl group follows the rotation of the one which is forced to rotate but in a highly irregular way. The rotation of methyl groups in protonated isobutene is considerably more complicated than in isobutene itself. The rotations of the three methyl groups are strongly coupled. Pitzer and Gwinn have published tables that can be used to calculate the contribution to energy from a hindered rotor.¹⁵ However, the existing theory for handling hindered rotors breaks down if there is more than one rotor and the rotors are not independent. A clear theoretical treatment of the situation in protonated isobutene can therefore not easily be given.

Upper and lower limits for the error introduced can, however, be suggested. As mentioned above the rotational barrier in the not-protonated isobutene is 9 kJ/mol. This is so high that computing the thermal energy contribution from the methyl groups under the assumption that there is only vibrational energy should not introduce a notable error. In protonated isobutene the contribution to the thermal energy due to vibration/rotation of the three methyl groups computed by the composite programs W1BD, G4, G3, and CBS is 2.3 + 2.15 + 1.55 ≈ 6 kJ/mol. As pointed out above the barrier for rotation may be very low. In the extreme case the methyl groups might behave like free rotors. Their contribution to the thermal energy would then be $3 \times 1/2RT \approx 4.0$ kJ/mol. The thermal energy of the protonated isobutene ion is therefore, in this case, overestimated by up to 2 kJ/mol. Correspondingly, the PA is then underestimated by the same amount. Neither of the extreme cases are likely, so the underestimation can probably be set to about 1.0 kJ/mol. Based on the best available theoretical calculation (W1BD) the PA of isobutene may well be 803.1 + 1.0 = 804.1 kJ/mol. This is the same value as is given by East et al., but they estimated the correction to be 2 kJ/mol and the uncorrected PA was 802.1 kJ/mol.¹⁴

The isobutene/*tert*-butyl cation couple is not the only species where there are methyl groups present and where vibrations/hindered rotation may be an issue. Rotational barriers have therefore been calculated at the B3LYP/6-31G(d) level. In the cases where experimental data are available in the cccbdb database a satisfactory agreement between calculated and experimental barriers are observed.¹⁶ The rotational methyl group barrier changes somewhat when a molecule is protonated. However, the changes appear to be small enough that taking it into account would only change the calculated PA by a few tenths of a kJ/mol. A detailed theoretical treatment seems difficult, in particular when there is more than one methyl group because there will be some interaction between the methyl groups and existing theory can only handle isolated hindered rotors.¹⁵

Zero Point Energy Correction. An equally important source of error in PA calculations may be the evaluation of the zero

point energy (ZPE). This is so because the sum of ZPEs from all vibrations is a large number. As an example, in dimethyl ether $\text{ZPE} = 238 \text{ kJ/mol}$, which means that an error as small as 0.2% leads to an error of 0.5 kJ/mol in the calculated proton affinity. The error might be even higher, but, on the other hand, one must keep in mind that because a PA calculation involves finding the enthalpy differences between the protonated and the unprotonated molecule an important cancellation of errors is likely because parts of the protonated and unprotonated molecule are virtually identical.

Some Further Comments on the Accuracy of the Proton Affinities. Corresponding comparisons of the computational accuracies of W1, G2, G3, and CBS-QB3 computational schemes have been carried out by Shields and co-workers.^{17,18} They studied deprotonation of neutral molecules, thereby forming anions. The compounds studied were chosen to be substances where the deprotonation enthalpies are stated to be known with an uncertainty less than 4.2 kJ/mol (1 kcal/mol). They also included computations at the CBS-APNO, B3P86, and PBE1PBE levels, which have not been applied in this work. Some molecules were even studied with computations at the CCSD(T)/aug-cc-PVNZ level with $N = 3, 4$, and 5.

As might be expected, it was found that all the above methods were in quite good agreement with the experimental values (*NIST Chemistry WebBook*, ref 1), with the computationally expensive methods CCSD(T) and W1 giving the best agreement. However, it was found that CCSD(T) and W1 in four or five cases gave deprotonation enthalpies that deviated more than 1 kcal/mol from the experimental values, thus indicating that even these very demanding methods do not quite reach the goal of chemical accuracy. At about the same time as Shields and co-workers published their computational work the concept "Active Thermochemical Tables" were published by Ruscic et al. at Argonne National Laboratory,¹⁹ which has led to a reassessment and a mostly small refinement of previously accepted thermodynamic data. The presently available list of enthalpies of formation is found on the Argonne National Laboratory Web site.²⁰ By means of the enthalpies of formation given in the list, new experimental deprotonation enthalpies may be calculated for the cases where deviations exceeding 1 kcal/mol were found by Shields and co-workers. The new experimental deprotonation values are not much different from those given in ref 1 which were used by Shields and co-workers,^{17,18} but with the new adjusted and more accurate values the deprotonation enthalpies calculated with the W1 scheme or CCSD(T) are within 1 kcal/mol from the experiment. The deprotonation study carried out by Shields and co-workers therefore corroborates the trustworthiness of W1 computations when protonation/deprotonation reactions are studied.

The Medium-Sized Molecules. The computational results on benzene and methylbenzenes are discussed here. The initial issue was as follows: Which of the composite methods G3B3 and CBS-QB3 is the more accurate. A glance at the numbers in Table 1 gives a clear answer. G3B3 gives results that concord very well with the accurate methods G4 and W1BD. The PAs calculated with CBS-QB3 are much too small whether they are compared with the other computational results or currently accepted experimental PAs like the NIST tables. The CBS-QB3 deviations from the other schemes and NIST values tend to increase with molecule size. The mean deviation from the PAs obtained from W1BD for the xylenes is 8.9 kJ/mol.

For the molecules where W1BD computations were carried out, benzene, toluene, and the xylenes, the methods W1BD, G4, and G3B3 are in excellent accord, as was also, generally, the case for the molecules discussed above. It should therefore be permissible to have confidence in the accuracy of the PA values computed by G4 and G3 for the molecules that are too big for W1BD computations. For the whole series from benzene to pentamethylbenzene the NIST PA values are four to five kJ/mol higher than the high-level theoretical results. Hexamethylbenzene is the only case where the NIST value agrees with the computational results.

As was discussed above for isobutene the computational schemes compute the thermal energies without making allowance for some vibrations possibly being hindered rotations. However, neglecting hindered rotations has consequences only if protonation leads to changes in rotational barriers, because, if not, the errors cancel. Barriers have been calculated at the B3LYP/6-31G(d) level.

Benzene has no methyl group, and the methyl group in toluene is practically a free rotor independent of protonation so neglecting hindered rotation has no consequences for these molecules.

The Xylenes. *p*-Xylene: In *p*-xylene the methyl groups are essentially free rotors. Upon protonation the two methyl groups are no more equivalent, and the rotational barrier for each methyl group must be discussed. The methyl group next to the protonation site retains a negligible rotation barrier, but the other methyl group experiences a barrier which is about 2.6 kJ/mol. According to the Pitzer and Gwinn tables¹⁵ this indicates that the calculated PA is about 0.5 kJ/mol too high when no correction for methyl group rotation is applied.

m-Xylene: The two methyl groups are again freely rotating. In the protonated molecule the two methyl groups are no more equivalent. The barriers are found to be 1.0 and 1.5 kJ/mol. The methyl groups are no more free rotors, but the barriers are well below the mean thermal energy and are almost negligible, but they indicate that the calculated PA may be 0.3 kJ/mol too high.

o-Xylene: In *o*-xylene the two methyl groups are no more free rotors. A rotational barrier 5.2 kJ/mol is found. After protonation the barriers for the two methyl groups are 3.2 and 6.7 kJ/mol. The errors introduced by the neglect of hindered rotation appear to cancel quite closely so the computational result does not seem to need any correction, but, if corrected, the PA might be increased about 0.1 kJ/mol.

Trimethylbenzenes. 1,3,5-Trimethylbenzene: In this case there is only one protonation site, and after protonation there are two nonequivalent methyl groups. In the nonprotonated molecule there is essentially free rotation. In the protonated ion one methyl group retains free rotation. The other two methyl groups which are in an ortho position relative to the protonated carbon atom are found to experience a rotational barrier of about 2 kJ/mol. According to the Pitzer and Gwinn tables this could imply that the thermal energy due to these two methyl groups may be $2 \times 0.3 = 0.6 \text{ kJ/mol}$ higher than it would be if the methyl groups were freely rotating. The computed PA of 1,3,5-trimethylbenzene may therefore be 0.6 kJ/mol too high when compared to a corrected PA value.

In 1,2,4-trimethylbenzene itself there is one freely rotating methyl group and two methyl groups which behave like the two methyl groups in *o*-xylene. Upon protonation ($\approx 95\%$ on C^5) only small changes in the rotational barriers are seen. The errors from treating the hindered rotor as a vibration will

therefore essentially cancel and there is probably no need for any correction.

The 1,2,3-trimethylbenzene is protonated mainly on C⁴. The methyl rotation barriers have not been evaluated, but it is to be expected that the barriers are not much changed by protonation so there is no clear indication for any correction to the calculated PA.

Tetramethylbenzenes. Only 1,2,4,5-tetramethylbenzene, durene, represents a simple case. In the unprotonated molecule the four methyl groups are equivalent. The two protonation sites are equivalent, and in the protonated molecule there are two different methyl groups. The methyl group rotation barrier in durene itself is 4.9 kJ/mol. In the protonated molecule the barriers have decreased to 2.5 and 3.5 kJ/mol. This suggests that the PA value obtained with G4 may be nearly 1 kJ/mol too low, but each of the methyl groups interacts with its neighbor so the Pitzer and Gwinn tables are not fully reliable.

Pentamethylbenzene: The system is too complex to allow a simple description. However, a few details may be pointed out. In the preceding methylbenzenes protonation does not take place on a carbon with a methyl group attached. In pentamethylbenzene it appears that up to 20% of the protons are on such carbon atoms. According to B3LYP/6-31G(d) based calculations the protonation then takes place on a carbon atom in meta position relative to the nonmethylated ring carbon atom (i.e., forming 1,2,3,4,5-pentamethyl-2H-benzene). There are three different CH₃ groups in both the protonated and unprotonated molecules. There are only moderate changes in the barriers for corresponding methyl groups. It cannot be concluded that the calculated PA needs a correction.

Hexamethylbenzene: Here the apparent rotation barrier is quite small, 1.5 kJ/mol, which seemingly indicates weakly hindered rotors. However, the methyl group rotations appear to be strongly coupled. When one methyl group is forced to rotate, the other methyl groups are subject to jerky rotational movements. Upon protonation, the rotation barriers for most of the methyl groups become considerably higher. The consequences for the PA are not easily quantified but may possibly be quite important. No further discussion seems warranted.

Summing up: No important corrections for the neglect of hindered rotations seem necessary. It appears to be allowed to conclude that the NIST WebBook PA values for the methylbenzenes are 4–5 kJ/mol too high. It should also be noted that the PA computations carried out with the M06-2X functional concord well with the Gn methods when methylbenzenes are studied. A look at the table shows that the mean absolute deviation from G4 is only 2.2 kJ/mol.

Zero Point Energy Correction. As mentioned earlier the ZPE is a large number so even a fractionally small error is important. However, an important cancellation of errors may be expected. The most important contributions to the ZPE come from the high frequency zero point vibrations, i.e. the C–H stretching frequencies as found in the methyl groups. They may be expected to be little influenced by protonation so there may be considerable error cancellation. The larger part of the remaining vibrations are also little influenced by protonation since most structural characteristics are only slightly perturbed. Still, the ZPE error may be more important than one would wish.

CONCLUSION

The proton affinities of a considerable number of molecules have been calculated theoretically by various high accuracy methods with results obtained by the W1 (W1BD) scheme forming an anchoring point for assessing the accuracy of G4, G3 (G3B3), CBS-QB3, and M06-2X. G4 and (mostly) G3B3 give within 2.0 kJ/mol the same result as W1BD (ketene excepted). CBS-QB3 computations were not satisfactory. They predict systematically too low PA values. The errors increase with molecule size. Calculations with the M06-2X functional show that rather large errors occur, but there is no systematic trend and the PAs of the methylbenzenes are in quite good accord with G4 and the mean absolute deviation is only 2.2 kJ/mol. The W1BD computations could only be extended up to xylenes. The other schemes have been extended to anthracene.

The computations strongly indicate that the PA of propene given by the NIST Tables (751.6 kJ/mol) should be reduced to 745.0 kJ/mol as given by W1BD and G4 computations. Also the NIST value for acetone (812.0 kJ/mol) seems to need a slight modification, to 815.4 kJ/mol, to agree with W1BD and G4. The PAs of methylbenzenes, as given by the NIST tables, appear to be, generally, 4 kJ/mol too high.

Possible needs for corrections to the calculated PAs caused by the neglect of hindered rotations of methyl groups have been qualitatively discussed. It is found that such corrections probably are less than ± 1 kJ/mol (except for penta- and hexamethylbenzene which could not be evaluated).

ASSOCIATED CONTENT

Supporting Information

The geometries and main computational results of the more time-consuming molecules and their protonated counterparts are given. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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