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MPW1K Performs Much Better than B3LYP in DFT Calculations on Reactions that Proceed by Proton-Coupled Electron Transfer (PCET)

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Abstract

DFT calculations have been performed with the B3LYP and MPW1K functional on the hydrogen atom abstraction reactions of ethenoxyl with ethenol and of phenoxyl with both phenol and α-naphthol. Comparison with the results of G3 calculations shows that B3LYP seriously underestimates the barrier heights for the reaction of ethenoxyl with ethenol by both proton-coupled electron transfer (PCET) and hydrogen atom transfer (HAT) mechanisms. The MPW1K functional also underestimates the barrier heights, but by much less than B3LYP. Similarly, comparison with the results of experiments on the reaction of phenoxyl radical with α-naphthol indicates that the barrier height for the preferred PCET mechanism is calculated more accurately by MPW1K than by B3LYP. These findings indicate that the MPW1K functional is much better suited than B3LYP for calculations on hydrogen abstraction reactions by both HAT and PCET mechanisms.

Many hydrogen atom abstraction reactions proceed by a classical hydrogen-atom transfer (HAT) mechanism, involving three electrons distributed among three atomic orbitals.[1] As shown schematically in Figure 1a, the proton and one of the electrons in the X-H bond being broken are both transferred to the singly occupied orbital on radical $Y^{\cdot}$.

However, in recent years both experimental and computational studies have found that, when the abstracting radical center carries at least one unshared pair of electrons and the hydrogen to be abstracted is bonded to an atom that also has an unshared pair of electrons, a proton-coupled electron transfer (PCET) mechanism may be preferred to a HAT mechanism.[2] As illustrated in Figure 1b, such a PCET mechanism involves a total of five atomic orbitals. The proton in the X-H bond is transferred to a lone pair of electrons on radical $Y^{\cdot}$; and, simultaneously, an electron is transferred from a lone pair on X to the singly occupied orbital on Y. Thus, unlike the case in HAT, where the proton and the electron of the hydrogen atom are transferred from X to the same AO on Y, in PCET the proton is transferred between one pair of AOs on X and Y, and the electron is transferred between another pair of AO on these two atoms.

We have reported the results of unrestricted (U)B3LYP calculations on the preferred mechanism for the degenerate hydrogen abstraction reactions of benzyl radical with toluene, methoxyl radical with methanol, and phenoxyl radical with phenol.[3] Our calculations found that for the first two of these reactions, a HAT mechanism is favored. However, for the reaction of phenoxyl with phenol, our (U)B3LYP calculations found a PCET mechanism to be

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preferred;[4] and we presented an analysis of why the mechanism of this reaction differs from that of the reaction of methoxyl with methanol.

Although Becke's three-parameter functional,[5] when combined with the correlation functional of Lee, Yang, and Parr,[6] usually gives good results for reactions of closed-shell molecules, the same is not true for reactions of radicals. Truhlar and coworkers have pointed out that (U) B3LYP calculations underestimate the barrier heights for a set of 40 HAT radical reactions, with a mean signed error of -4.8 kcal/mol.[7] In the same paper Truhlar *et al.* showed that MPW1K -- a modified version of the Perdew-Wang gradient-corrected exchange functional, with one parameter optimized to give the best fit to the kinetic data for these 40 radical reactions, -- reduced the mean signed error in the barrier heights for these reactions to -1.3 kcal/mol.

It is not known whether B3LYP makes similar or, perhaps, even larger errors for PCET reactions, as for these 40 HAT reactions. It is also not known whether MPW1K is more or less accurate than B3LYP in computing the barrier heights for PCET reactions.

In order to assess how well these two functionals perform in calculations on a PCET reaction, we have carried out calculations on the degenerate abstraction of the hydroxyl hydrogen of ethenol (the enol of ethanal) by ethenoxyl radical via a PCET mechanism.

$$H_2C{=}CH-OH+\cdot O-CH{=}CH_2 - - - > H_2C{=}CH-O\cdot +HO-CH{=}CH_2 \qquad (1)$$

We chose this very simple reaction because we wanted to be able to compare the performance of both B3LYP and MPW1K against that of a high-quality *ab initio* method, which could be anticipated to give reliable results. For this purpose we selected the G3 method.[8]

In this manuscript we report a comparison of the results of (U)B3LYP and (U)MPW1K DFT calculations with the results of G3 calculations for computing the HAT and PCET barrier heights for O-H hydrogen abstraction from ethenol by ethenoxyl radical. We have also computed the (U)MPW1K barrier heights for both types of mechanisms in the reaction of phenol with phenoxyl radical, which we studied previously with (U)B3LYP calculations;[3] and, in addition, we have performed (U)MPW1K and (U)B3LYP calculations on the reaction of phenoxyl radical with α-naphthol. For the last of these three reactions we report a comparison of the (U)MPW1K and the (U)B3LYP computational results with the experimental results obtained by Foti, Ingold, and Lusztyk.[9]

Computational Methodology

Truhlar and coworkers used the 6-31+G(d,p) basis set[10] in their comparisons of the B3LYP and MPW1K functionals;[7] so we elected to use the same basis set in this study for both types of DFT calculations. We also carried out single-point (U)B3LYP and (U)MPW1K calculations with the aug-cc-pVTZ basis set on the reaction of ethenoxyl radical with ethanol.[11]

The geometries of the stationary points for the G3 calculations were obtained by performing (U)B3LYP calculations with the 6-31G(d) basis set.[12] Unrestricted wave functions were used for all of the calculations on radicals. Geometries were optimized, transition structures located, and vibrational analyses performed using the Gaussian03 package of electronic structure programs.[13] The unscaled vibrational frequencies were used to obtain the zero-point energies and heat capacities that were necessary in order to convert the differences in electronic energies into differences in enthalpies at 298 K.

Results and Discussion

Hydrogen Abstraction from Ethenol by Ethenoxyl Radical

Figure 2 gives the most important bond lengths and bond angles in ethenol, ethenoxyl, the hydrogen-bonded complex formed from them, and the transition structure for abstraction of the hydroxyl hydrogen of the alcohol by the oxygen of the radical. (U)MPW1K/6-31+G(d,p), (U)B3LYP/6-31+G(d,p), and (U)B3LYP/6-31G(d) geometrical parameters are all provided.[14] Complete descriptions of all the optimized geometries are available in the Supporting Information.

PCET, via a planar transition structure, was found to be the preferred mechanism for hydroxyl hydrogen abstraction from ethenol by ethenoxyl. In the C_{2h} transition structure, as the proton in the hydrogen-bonded complex is transferred from ethanol to a σ lone pair in ethenoxyl, a π electron is transferred from the alcohol to the radical.

Attempts to find the transition structure for hydrogen abstraction by a HAT mechanism were unsuccessful. In order to estimate what the energy of such a transition structure would be, we optimized a partially constrained geometry in C_i symmetry. In this “transition structure” the double bonds were constrained to planarity (i.e. the H-C-C-H and H-C-C-O dihedral angles were frozen at 0° or 180°) and the C=C-O-O dihedral angle was fixed at 90°. The most important bond lengths and bond angles in the (U)B3LYP and (U)MPW1K geometries, optimized with these constraints, are also given in Figure 2; and a full description is provided in the Supporting Information.

The relative energies (and enthalpies) at the (U)B3LYP, (U)MPW1K and G3 levels of theory of the separated reactants, hydrogen-bonded complex, PCET transition structure (TS) and the partially constrained C_i geometry (HAT C_i “TS”) are shown graphically in Figure 3. The results given in this figure reveal that, with the 6-31+G(d,p) basis set, (U)B3LYP and (U)MPW1K give nearly the same energy as the G3 calculations for the strength of the hydrogen-bond formed between ethenol and ethenoxyl. However, with the larger aug-cc-pVTZ basis set, the (U) B3LYP and (U)MPW1K energies of the hydrogen-bonded complex, relative to the isolated reactants, are both about 1 kcal/mol higher than the G3 energy.

Although, relative to the isolated reactants, (U)B3LYP and (U)MPW1K give very similar energies for the hydrogen-bonded complex between ethanol and ethenoxyl, the PCET TS and the constrained HAT “TS” are calculated to be, respectively, 9.7 and 7.5 kcal/mol lower in energy by (U)B3LYP/6-31+G(d,p) than by (U)MPW1K/6-31+G(d,p). Calculations with the aug-cc-pVTZ basis set give nearly the same differences between the (U)B3LYP and MPW1K results as the calculations with the 6-31+G(d,p) basis set. Obviously, hydroxyl hydrogen abstraction from ethenol by ethenoxyl, by either a PCET or HAT mechanism, is predicted to be much more facile by (U)B3LYP than by(U)MPW1K.

We assume that the G3 calculations give reliable results for the hypothetical model reaction of ethenoxyl with ethenol. If this assumption is valid, the G3 results, which are also shown graphically in Figure 3, indicate that (U)MPW1K gives a much more realistic estimate of the PCET and HAT barrier heights than does (U)B3LYP.

For the PCET mechanism, the G3 barrier height of $\Delta H^{\ddagger} = 12.9$ kcal/mol, relative to the isolated reactants, is 13.1 kcal/mol higher than the (U)B3LYP/6-31+G(d,p) barrier height, but only 3.4 kcal/mol higher than the (U)MPW1K/6-31+G(d,p) barrier height. Thus, it appears that (U) B3LYP and (U)MPW1K both underestimate the PCET barrier height; but (U)B3LYP underestimates it by much more than (U)MPW1K.[15]

(U)B3LYP, (U)MPW1K, and G3 all find that the HAT “TS” is considerably higher in energy than the PCET TS. This qualitative agreement lends credence to the preference for a PCET over a HAT mechanism, which is predicted for the hypothetical reaction of ethenol with ethenoxyl by all three computational methods.

Hydrogen Abstraction from Phenol by Phenoxyl Radical

The finding that (U)MPW1K apparently gives much more accurate results than (U)B3LYP for hydrogen abstraction from ethenol by ethenoxyl led us to reinvestigate hydrogen abstraction from phenol by phenoxyl, using (U)MPW1K/6-31+G(d,p) calculations. The (U)MPW1K results are shown graphically in Figure 4. For comparison, the results that we previously obtained at the (U)B3LYP/6-31G(d) level of theory,[3] as well as (U)B3LYP/6-31+G(d,p) results, are also shown in Figure 4.

Both sets of DFT calculations find that the PCET transition structure is lower in energy than the C_{2h} constrained HAT “TS”. The energy difference is computed to be 4.6 kcal/mol by (U) MPW1K/6-31+G(d,p), 6.1 kcal/mol by (U)B3LYP and the same basis set, and 7.1 kcal/mol by (U)B3LYP/6-31G(d). Using the 6-31+G(d,p) basis set, the two functionals place the hydrogen-bonded complex between phenoxyl and phenol below the isolated reactants by almost exactly the same energy and enthalpy.

As shown in Figure 4, the major difference between the results obtained with the two functionals is in the enthalpy that is computed to be required in order to pass over the PCET TS. Starting from the isolated reactants, the activation enthalpy for the PCET reaction of phenoxyl with phenol is predicted to be 8.2 kcal/mol lower by (U)B3LYP/6-31+G(d,p) calculations than by (U)MPW1K/6-31+G(d,p). This difference in predicted barrier heights is only 15% smaller than the difference of 9.7 kcal/mol between the (U)B3LYP/6-31+G(d,p) and (U)MPW1K/6-31+G(d,p) values of $\Delta H^{\ddagger}$ for the PCET reaction of ethenol with ethenoxyl.

Hydrogen Abstraction from α-Naphthol by Phenoxyl Radical

The activation parameters for degenerate hydrogen exchange between phenol and phenoxyl have not been measured; so a comparison of the very different values of $\Delta H^{\ddagger}$, predicted by (U) B3LYP and (U)MPW1K, with an experimental value is not possible. However, the exothermic abstraction of the hydroxyl hydrogen atom from α-naphthol by phenoxyl radical has been found to have $E_a = 2.2 \pm 0.3$ kcal/mol and log A = 8.9 ± 0.3 kcal/mol.[9] Therefore, we performed calculations on this reaction, in order to assess how well (U)B3LYP and (U)MPW1K do in calculating the activation enthalpy for it.

As shown in Figure 5, (U)B3LYP/6-31+G(d,p) predicts a PCET TS energy that is 7.8 kcal/mol lower than that computed by (U)MPW1K/6-31+G(d,p). (U)B3LYP unequivocally predicts a barrierless reaction between phenoxyl and α-naphthol. If this bimolecular reaction really were barrierless, it would be expected to be found experimentally to have a negative energy of activation[16] rather than the small but positive value measured by Foti, Ingold, and Lusztyk.[9]

In contrast to (U)B3LYP, (U)MPW1K predicts an activation energy that is in very good agreement with the value of $E_a = 2.2 \pm 0.3$ kcal/mol, reported by Foti, Ingold, and Lusztyk,[9] because the calculated activation enthalpy should be based on the isolated reactants, rather than on the hydrogen-bonded complex between them.[17,18] After converting the (U)MPW1K/6-31+G(d,p) value of $\Delta H^{\ddagger} = 1.5$ kcal/mol for the isolated reactants to $E_a = 2.7$ kcal/mol, the (U) MPW1K activation energy is within 0.5 kcal/mol of the experimental value.

Conclusions

Comparison of the results of (U)B3LYP and (U)MPW1K calculations on the reaction of ethenoxyl with ethenol with the results obtained by G3 calculations shows that all three methods find a PCET reaction mechanism to be favored over a HAT mechanism. However, the G3 results indicate that the enthalpies of activation, computed by DFT with these two functionals, are too low for both the PCET and HAT reaction mechanisms.

Nevertheless, the errors in barrier heights made by (U)MPW1K are much smaller than those made by (U)B3LYP. For example, for the favored PCET mechanism for the reaction of ethenoxyl with ethenol, the (U)MPW1K/6-31+G(d,p) enthalpy of activation is 9.7 kcal/mol closer than the (U)B3LYP/6-31+G(d,p) value to the G3 value of $\Delta H^{\ddagger}$ = 12.9 kcal/mol. Similarly, the barriers to the PCET reactions of phenoxyl radical with phenol and with α-naphthol are calculated by (U)MPW1K/6-31+G(d,p) to be higher than those predicted by (U) B3LYP/6-31+G(d,p) by, respectively, 8.2 and 7.8 kcal/mol. The (U)MPW1K activation energy of E_a = 2.7 kcal/mol for the latter reaction is in excellent agreement with the experimental value of E_a = 2.2 ± 0.3 kcal/mol.

Since several recent studies of PCET reactions have been based on (U)B3LYP calculations,[3,4a-c,g] the barrier heights for these reactions were almost certainly underestimated by the calculations. For future DFT calculations on PCET reactions, the use of Truhlar's MPW1K functional is strongly recommended by the results reported here, because MPW1K is likely to provide much more reliable results than use of B3LYP.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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(14). Selected geometries were also reoptimized with the 6-311+G(2df,2p) basis set. However, the relative (U)MPW1K and (U)B3LYP energies at these geometries were essentially the same as the single-point aug-cc-pVTZ energies, computed at the geometries optimized with the 6-31+G(d,p) basis set.

(15). It should be recalled that MPW1K also underestimated the barrier heights in the 40-reaction test set used by Truhlar and coworkers, but B3LYP underestimated the barrier heights by nearly four times as much as MPW1K.[7]

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(17). Although MPW1K predicts that the enthalpy of the hydrogen-bonded complex is 6.7 kcal/mol lower than that of the isolated reactants, the complex is also calculated to be lower in entropy by 28.1 cal/mol-K. Thus, at 298 K, $\Delta G = 1.7$ kcal/mol for complex formation; and the equilibrium constant, in terms of mole fractions of phenoxyl, α-naphthol, and the hydrogen bonded complex formed from them is $K = 5 \times 10^{-2}$. In the solvent mixtures used by Foti, Ingold, and Lusztyk the equilibrium constant for concentrations, expressed in mol/L, is about a factor of 10 smaller than the value for mole fractions. The highest concentrations of α-naphthol used were 0.3 M; so under these conditions the ratio of hydrogen bonded complex to free phenoxyl radical would have been on the order of 10^{-4}. There are obvious inaccuracies in using an enthalpy and entropy, computed for the gas-phase, to calculate the equilibrium constant for hydrogen-bonded complex formation in the solvent mixtures used in ref. [9]. Nevertheless, the very small equilibrium constant that we do obtain provides good reason to believe that the phenoxyl does not react with α-naphthol in an irreversibly formed hydrogen-bonded complex between them. Instead, our calculations predict that complex formation is reversible, so that the overall enthalpy of activation should be based on the free reactants, rather than on the hydrogen-bonded complex between them.

(18). A bimolecular reaction between phenoxyl and α-naphthol, rather than a unimolecular reaction of an irreversibly formed hydrogen-bonded complex, is more consistent with the experimental value of $\log A = 8.9 \pm 0.3$ for the reaction.[9]

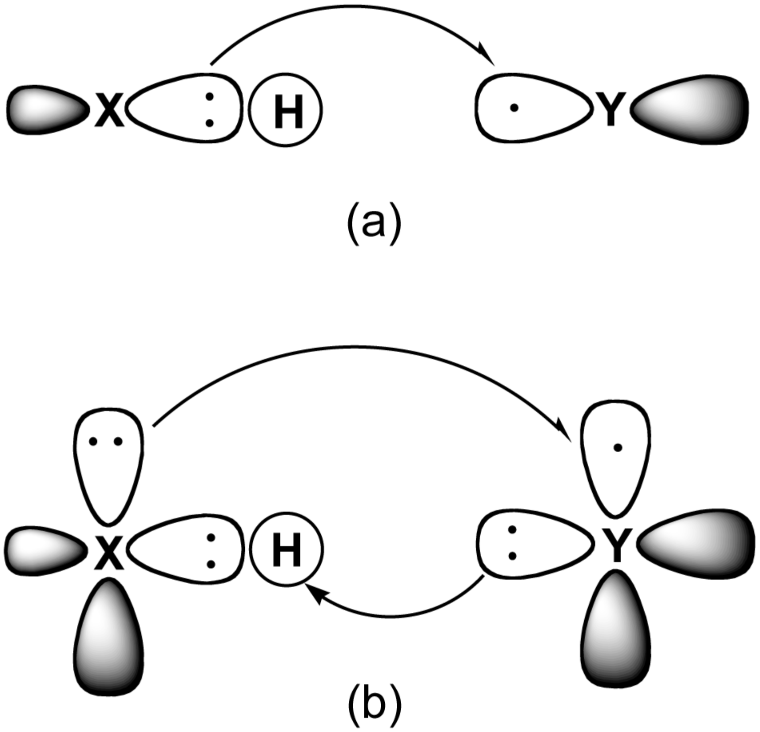

Figure 1.

Schematic depiction of (a) hydrogen atom transfer (HAT) and (b) proton-coupled electron transfer (PCET) mechanisms for abstraction of a hydrogen atom from an X-H bond by radical Y˙.

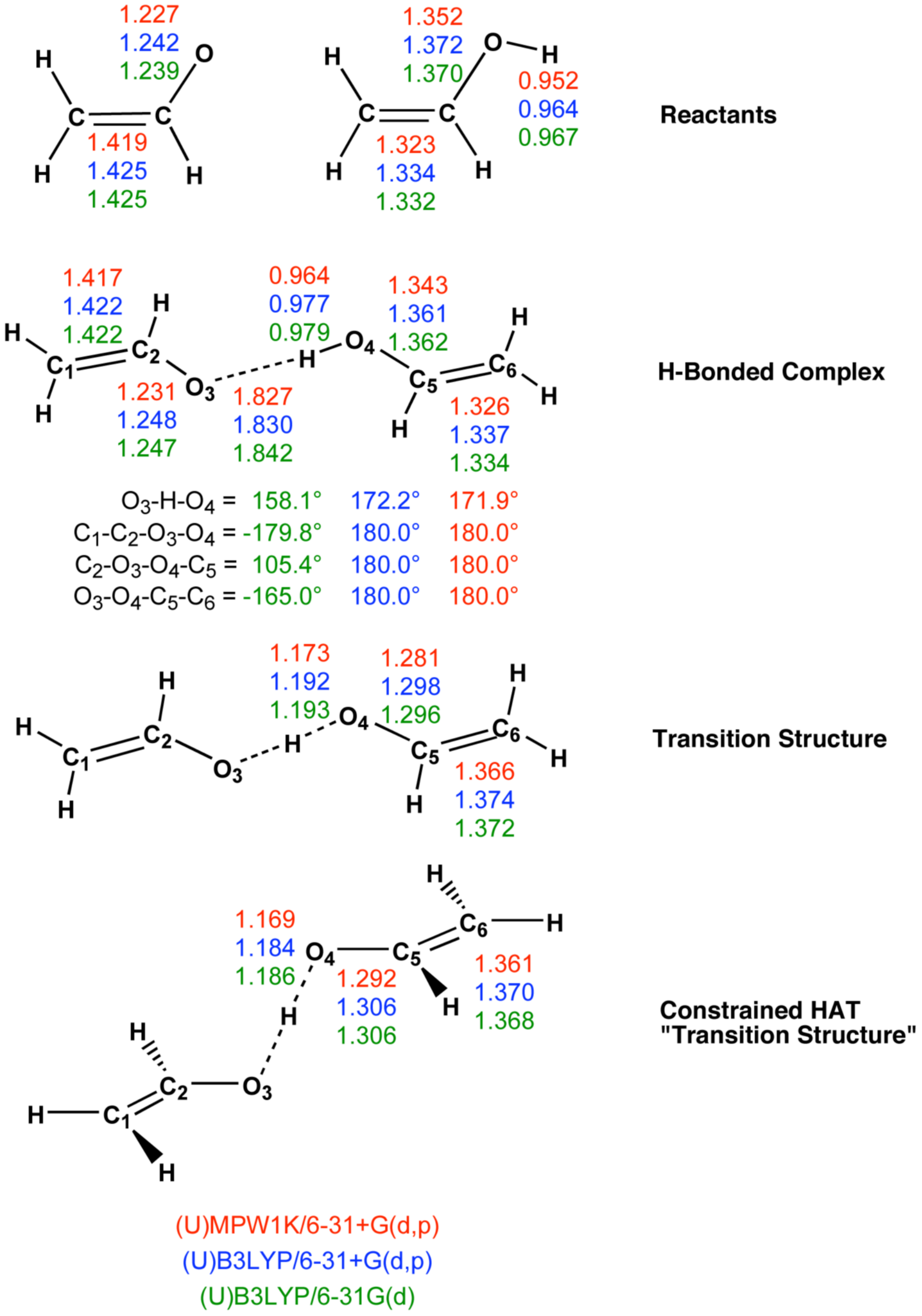

Figure 2.

Important geometrical parameters of the stationary points, located by three different types of calculations, in the reaction between ethenoxyl and ethanol.

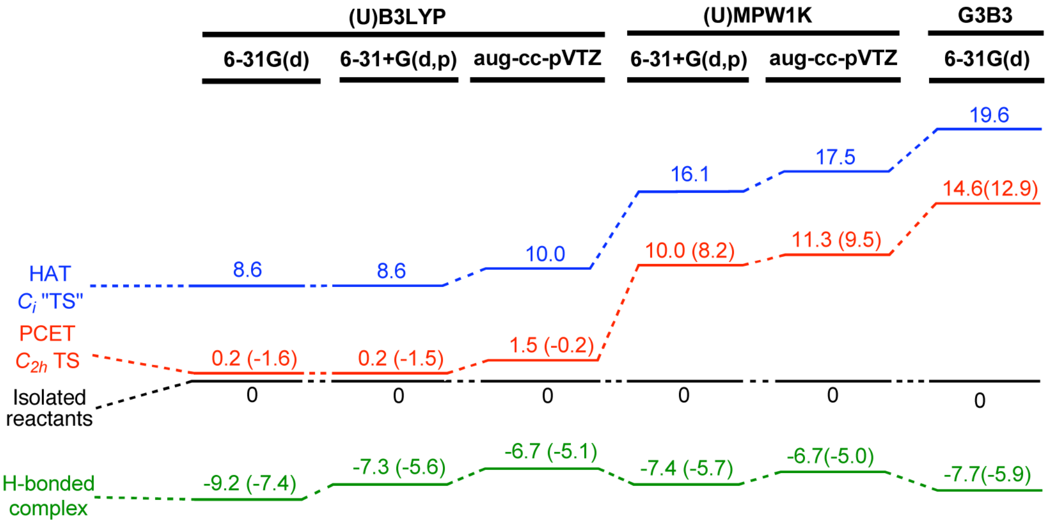

Figure 3.

Relative energies (and enthalpies) of stationary points, computed by different methods with different basis sets, for the reaction between ethenoxyl and ethenol. The designation G3B3/6-31G(d) means that the geometries for the G3 calculations were optimized with the (U) B3LYP functional and the 6-31G(d) basis set. Using the results of (U)B3LYP/6-31G(d) vibrational analyses, zero-point and heat capacity corrections were removed from the G3 enthalpies, so that the purely electronic energies of the PCET TSs and the constrained HAT C_i “TSs” could be compared, not only at the (U)B3LYP and (U)MPW1K levels of theory, but also at the G3 level.

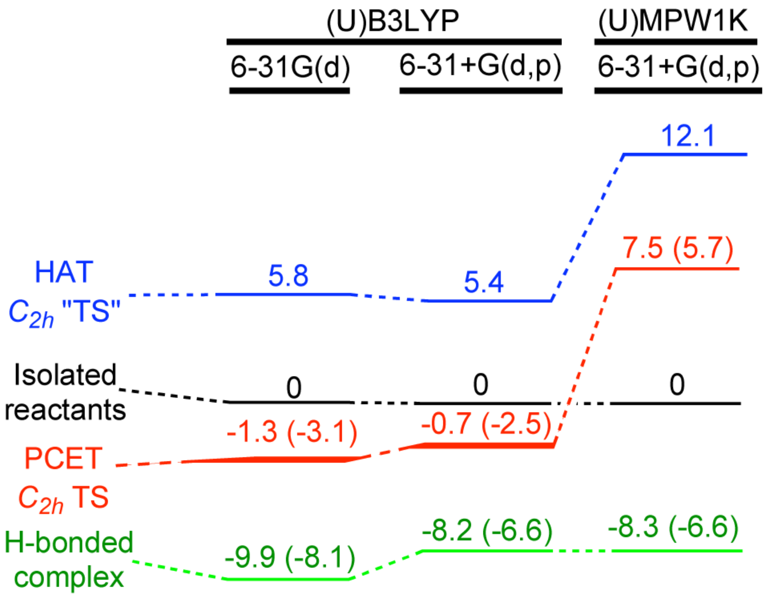

Figure 4.

Relative energies (and enthalpies) of stationary points, computed by (U)B3LYP/6-31G(d), (U)B3LYP/6-31+G(d,p), and (U)MPW1K/6-31+G(d,p), for the reaction between phenoxyl and phenol.[3]

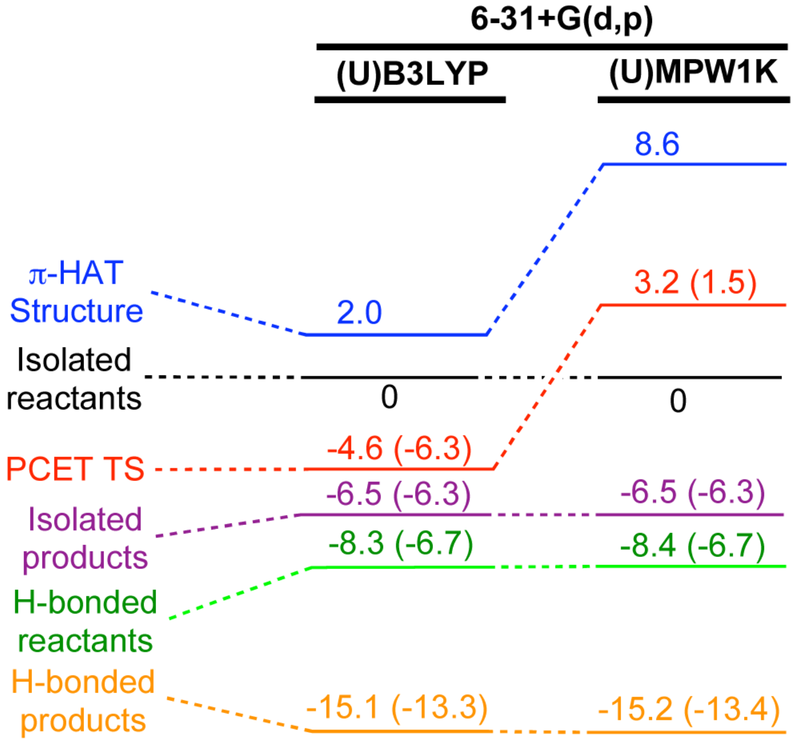

Figure 5.

Relative energies (and enthalpies) of stationary points, computed by (U)B3LYP/6-31+G(d,p) and by (U)MPW1K/6-31+G(d,p), for the reaction between phenoxyl and α-naphthol.