Computation of ionization potential of conjugated radicals by hybrid density functional theory methods

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The ionization potential for the vinyl, allyl, but-2-enyl, benzyl, *p*-methoxybenzyl and *p*-cyanobenzyl radicals have been calculated by *ab initio* and hybrid density functional theory (DFT) methods. Four hybrid DFT methods (BHandH, BHandHLYP, Becke3LYP and Becke3P86) have been applied and the computed ionization potentials are compared with *ab initio* (ROHF and MP2) computed and experimentally determined values. The suitability of hybrid DFT methods for computing the ionization potentials of conjugated radicals is discussed, while Becke3P86/6-31 + G(d) is selected as a reliable theoretical model for this study.

Introduction

The calculation of physical and chemical properties of conjugated radicals is a very hard computational problem. The broadly used *ab initio* methods, as an approach to generate very accurate data, usually fail.[1] Nowadays density functional (DFT) methods[2] are becoming increasingly popular tools for solving theoretical chemistry problems. The DFT methods are less time consuming because they use the more economic Kohn–Sham approach.[3] We investigated the suitability of DFT methods for computed *ab initio* hard-to-handle problems like the geometries and energies of the NO dimer,[4] nitrogen oxides,[5] nitrogen fluorides,[6] nitrogen oxide–nitrogen fluoride,[7] sulfur fluorides,[8] sulfuroxy halides,[9] phosphorous fluorides[10] and the hydrogen radical displacement reaction with a fluorine radical on the hydrogen molecule.[11] In all of these studies excellent agreement was obtained between the experimental and computed geometries and energies. We also applied DFT methods for computing the activation energies of the cycloaddition reactions for ethene with butadiene and cyclopentadiene.[12] The obtained activation energies with hybrid DFT methods differ from the experimental values by only 1–2 kcal mol^{-1}.[†] In a continuation of this study we have shown that the optimization of the geometries of the reactants and the transition-state structures is not even necessary with hybrid DFT methods.[13] If the geometries are optimized by AM1 semiempirical methods and the energy evaluated with the Becke3LYP/6-31G* hybrid DFT model, almost identical energies are obtained as with full DFT optimization. This interesting approach has been successfully used to compute the activation energies for organic reactions that involve large organic molecules that otherwise would require sizable computational resources.[14] This excellent correlation between computed values and experimentally determined geometries and activation barriers led us to direct our research to other problems which are more arduous to compute; one such problem is the evaluation of the ionization potentials for aliphatic radicals.[15] Excellent agreement between computed and experimentally determined ionization potentials for the methyl radical was obtained with the Becke3LYP method, while for all other aliphatic radicals the best results were obtained with Becke3P86 hybrid DFT methods. There is little, if any at all, basis set sensitivity in computing ionization potentials. Furthermore, the calculated ionization potentials on AM1 geometries are almost identical to those obtained with full DFT calculations. We selected the Becke3LYP/6-31 + G(d) hybrid DFT model as the one that is the most reliable for computing ionization potentials. Here we are extending our approach for computing the ionization potential of conjugated organic radicals.

Theoretical methods

All calculations were performed with the GAUSSIAN 92[16] implementation of density functional theory and the MOPAC 6.0[17] implementation of the AM1 semiempirical method.[18] The optimizations were performed without any geometry restrictions using the Fletcher–Powell[19] method and the default GAUSSIAN convergence criteria. Four different hybrid DFT methods were used: BHandH, which is Becke's half-and-half method that incorporates a gradient corrected correlation functional with an exchange functional formed from equal parts of the Hartree–Fock and its gradient-corrected exchange terms,[20] BHandHLYP, which is Becke's half-and-half method with LYP[21] correlation added, Becke's 3 parameter functional[22] with the non-local correlation provided by the LYP[21] expression and Becke3P86, which is Becke's 3 parameter functionals[22] with non-local correlation by the Perdew 86 expression.[23]

Results and discussion

Although the vinyl radical is not conjugated, we chose this molecule with the intention of observing whether the hybrid DFT method can handle the system with a perpendicular π-bond, since the Becke3P86/6-31 + G(d) model correctly predicts the ionization energy for the ethyl radical.[15] Full *ab initio* (ROHF and MP2) calculations predicted the ionization potentials considerably below experimentally obtained values (Table 1). All four hybrid DFT methods applied predict better ionization potentials than obtained with the *ab initio* methods. For the case of aliphatic radicals the best results are obtained with the Becke3LYP hybrid DFT method (Table 1). As mentioned above, we demonstrated that the computation of the ionization potential with Becke3P86 based on AM1 radical geometries produces results that are equal to those obtained with full DFT calculation.[15] We tested this approach to estimate the ionization potential of the vinyl radical (Table 2) The computed results are less accurate than with full DFT calculations. For example, full Becke3P86/6-31 + G* predicts the ionization potential for the vinyl radical to be 9.32 eV, while with calculations based on AM1 geometry it is predicted to be 9.21 eV, which is further from the experimental value of 9.45 eV.[24] Nevertheless, this approach should be considered when

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[†] 1 cal = 4.184 J.

Table 1 Total energies (au)‡ and ionization potentials (eV) for the vinyl radical calculated by using the 6-31 + G(d) basis set

Method	$E_{\text{vinyl radical}}$	$E_{\text{vinyl cation}}$	$E_{\text{SOMO}}{}^{a}$	$E_{\text{i,a}}{}^{b}$	$E_{\text{i,b}}{}^{c}$
ROHF	−77.385 722 8	−77.087 275 1	−0.091 37	8.12	2.29
BHandH	−77.261 811 2	−76.949 422 2	−0.295 09	8.50	8.03
BHandHLYP	−77.853 947 9	−77.534 936 4	−0.305 52	8.68	8.31
Becke3LYP	−77.907 860 2	−77.586 842 4	−0.244 23	8.74	6.65
Becke3P86	−78.172 025 0	−77.829 413 8	−0.265 76	9.32	7.23
MP2	−77.611 041 8	−77.308 328 6	−0.400 93	8.24	10.91
Exp.[24]				9.45(5)	9.45(5)

[a] E_{SOMO} = total energy of the singly occupied molecular orbital. [b] $E_{\text{i,a}}$ = ionization potential calculated as the difference in energy of the methyl cation and methyl radical. [c] $E_{\text{i,b}}$ = ionization potential calculated from the SOMO.

Table 2 Total energies (au) and ionization potentials (eV) for vinyl radicals calculated with AM1 geometries by using the 6-31 + G(d) basis set

Method	$E_{\text{vinyl radical}}$	$E_{\text{vinyl cation}}$	$E_{\text{SOMO}}{}^{a}$	$E_{\text{i,a}}{}^{b}$	$E_{\text{i,b}}{}^{c}$
ROHF	−77.373 934 2	−77.081 982 1	−0.066 94	7.94	1.82
BHandH	−77.255 288 4	−76.946 503 9	−0.259 79	8.40	7.07
BHandHLYP	−77.846 750 5	−77.531 421 7	−0.268 37	8.58	7.30
Becke3LYP	−77.901 590 6	−77.584 813 2	−0.284 81	8.62	7.75
Becke3P86	−78.165 771 3	−77.827 405 0	−0.232 54	9.21	6.33
MP2	−77.603 084 0	−77.305 969 3	−0.359 30	8.08	9.78
Exp.[24]				9.45(5)	9.45(5)

[a] E_{SOMO} = total energy of the singly occupied molecular orbital. [b] $E_{\text{i,a}}$ = ionization potential calculated as the difference in energy of the methyl cation and methyl radical. [c] $E_{\text{i,b}}$ = ionization potential calculated from the SOMO.

Table 3 Total energies (au) and ionization potentials (eV) for the allyl radical calculated by using the 6-31 + G(d) basis set

Method	$E_{\text{allyl radical}}$	$E_{\text{ally cation}}$	$E_{\text{SOMO}}{}^{a}$	$E_{\text{i,a}}{}^{b}$	$E_{\text{i,b}}{}^{c}$
ROHF	−116.448 723 2	−116.194 335 8	−0.071 27	6.92	1.94
BHandH	−116.302 103 1	−116.013 328 6	−0.245 83	7.86	6.69
BHandHLYP	−117.187 636 0	−116.895 294 6	−0.252 29	7.96	6.87
Becke3LYP	−117.267 921 0	−116.973 481 1	−0.203 54	8.01	5.54
Becke3P86	−117.678 191 4	−117.361 129 8	−0.226 14	8.63	6.15
MP2	−116.819 168 4	−116.546 420 7	−0.334 60	7.42	9.11
Exp.[24]				8.16(3)	8.16(3)

[a] E_{SOMO} = total energy of the singly occupied molecular orbital. [b] $E_{\text{i,a}}$ = ionization potential calculated as the difference in energy of the methyl cation and methyl radical. [c] $E_{\text{i,b}}$ = ionization potential calculated from the SOMO.

Table 4 Total energies (au) and ionization potentials (eV) for the allyl radical calculated with AM1 geometry by using the 6-31 + G(d) basis set

Method	$E_{\text{allyl radical}}$	$E_{\text{allyl cation}}$	$E_{\text{SOMO}}{}^{a}$	$E_{\text{i,a}}{}^{b}$	$E_{\text{i,b}}{}^{c}$
ROHF	−155.482 933 6	−155.247 056 3	−0.061 70	6.42	1.68
BHandH	−155.300 407 0	−155.034 616 5	−0.227 01	7.23	6.18
BHandHLYP	−156.477 088 2	−156.206 151 0	−0.234 08	7.37	6.37
Becke3LYP	−156.585 988 0	−156.315 575 0	−0.185 31	7.36	5.04
Becke3P86	−157.143 146 6	−156.850 434 3	−0.207 78	7.97	5.65
MP2	−155.987 804 2	−155.736 659 7	−0.313 97	6.83	8.54
Exp.[24]				8.16(3)	8.16(3)

[a] E_{SOMO} = total energy of the singly occupied molecular orbital. [b] $E_{\text{i,a}}$ = ionization potential calculated as the difference in energy of the methyl cation and methyl radical. [c] $E_{\text{i,a}}$ = ionization potential calculated from the SOMO.

the ionization potential for large organic molecules needs to be calculated.

For the conjugated radicals considered here, the allyl radical shares an analogy in behaviour with the substituted methyl radicals, which were studied previously.[15] The ROHF/6-31 + G(d) and MP2/6-31 + G(d) *ab initio* calculations predict the ionization potential to be 6.92 and 7.42 eV, respectively. The values are considerably below 8.16 eV, as determined experimentally[24] (Table 3). We further tested these methods for the calculation of ionization potentials using the combination of DFT calculation on AM1 geometries (Table 4). As in all our previous studies, we achieved excellent agreement with the experimental results. Now the Becke3P86 method produces results that are closest to the experimental values (Table 4). At this moment we do not have a satisfactory explanation for this discrepancy, as for predicting the ionization potential with full DFT calculations *versus* the ionization potential calculated on AM1 geometry for the allyl radical. However, this approach, as used previously by us for the study of aliphatic radicals, seems to be acceptable for allyl radicals also.

To investigate further the capability of hybrid DFT methods to compute correctly the ionization potentials of allylic conjugated radicals, we calculated the ionization potential for the but-2-enyl radical (Table 5). Here, as in the rest of the paper, the geometries are optimized with the AM1 semiempirical

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‡ 1 au = 4.360 × 10^{-18} J.

Table 5 Total energies (au) and ionization potentials (eV) for the but-2-enyl radical calculated with AM1 generated geometry by using the 6-31 + G(d) basis set

Method	$E_{\text{but-2-enyl radical}}$	$E_{\text{but-2-enyl cation}}$	E_{SOMO}[a]	$E_{\text{i.a}}$[b]	$E_{\text{i.b}}$[c]
ROHF	− 155.482 933 6	− 155.247 056 3	− 0.061 70	6.42	1.68
BHandH	− 155.300 407 0	− 155.034 616 5	− 0.227 01	7.23	6.18
BHandHLYP	− 156.477 088 2	− 156.206 151 0	− 0.234 08	7.37	6.37
Becke3LYP	− 156.585 988 0	− 156.315 575 0	− 0.185 31	7.36	5.04
Becke3P86	− 157.143 146 6	− 156.850 434 3	− 0.207 78	7.96	5.65
MP2	− 155.987 804 2	− 155.736 659 7	− 0.313 97	6.83	8.54
Exp.[24]				7.71(5)	7.71(5)

[a] E_{SOMO} = total energy of the singly occupied molecular orbital. [b] $E_{\text{i,a}}$ = ionization potential calculated as the difference in energy of the methyl cation and methyl radical. [c] $E_{\text{i,b}}$ = ionization potential calculated from SOMO.

Table 6 Total energies (au) and ionization potentials (eV) for the benzyl radical calculated with AM1 generated geometry by using the 6-31 + G(d) basis set

Method	$E_{\text{benzyl radical}}$	$E_{\text{benzyl cation}}$	E_{SOMO}[a]	$E_{\text{i.a}}$[b]	$E_{\text{i.b}}$[c]
ROHF	−269.117 528 4	−268.884 632 6	− 0.070 08	6.34	1.91
BHandH	−268.802 758 5	−268.543 699 5	− 0.227 89	7.05	6.20
BHandHLYP	−270.752 163 3	−270.489 638 7	− 0.232 88	7.14	6.34
Becke3LYP	−270.925 639 6	−270.664 208 0	− 0.189 17	7.11	5.15
Becke3P86	−271.804 116 5	−271.519 702 6	− 0.212 22	7.74	5.77
Exp.[24]				7.75(8)	7.75(8)

[a] E_{SOMO} = total energy of the singly occupied molecular orbital. [b] $E_{\text{i,a}}$ = ionization potential calculated as the difference in energy of the methyl cation and methyl radical. [c] $E_{\text{i,b}}$ = ionization potential calculated from the SOMO.

Table 7 Total energies (au) and ionization potentials (eV) for the *p*-cyanobenzyl radical calculated with AM1 generated geometry by using the 6-31 + G(d) basis set

Method	$E_{p\text{-cyanobenzyl radical}}$	$E_{p\text{-cyanobenzyl cation}}$	E_{SOMO}[a]	$E_{\text{i.a}}$[b]	$E_{\text{i.b}}$[c]
ROHF	−360.852 735 3	−360.594 551 3	− 0.089 96	7.03	2.45
BHandH	−360.426 241 2	−360.143 475 6	− 0.254 25	7.69	6.92
BHandHLYP	−362.948 602 1	−362.662 622 1	− 0.259 08	7.78	6.92
Becke3LYP	−363.173 522 3	−362.890 850 4	− 0.215 19	7.69	5.86
Becke3P86	−364.258 360 5	−363.952 439 6	− 0.238 57	8.33	6.49
Exp.				8.58(10)	8.58(10)

[a] E_{SOMO} = total energy of the singly occupied molecular orbital. [b] $E_{\text{i,a}}$ = ionization potential calculated as the difference in energy of the methyl cation and methyl radical. [c] $E_{\text{i,b}}$ = ionization potential calculated from the SOMO.

method and the ionization potential is calculated by both *ab initio* and DFT methods using these geometries. All the calculated values are as expected. The ROHF as well as MP2 *ab initio* methods drastically underestimated the ionization potential for the but-2-enyl radical (by 1.29 and 0.88 eV, respectively). Again, every hybrid DFT method produces much better results than both *ab initio* methods. The Becke3P86 produces an ionization potential that is satisfactory (0.25 eV different to the experimental value). The hybrid Becke3P86 DFT methods produce reliable ionization potentials for allylic radicals. In all of our calculations the energies of the singly occupied molecular orbital (SOMO) predicted by both *ab initio* and hybrid DFT methods poorly estimate the ionization energy for aliphatic radicals,[15] this is also demonstrated here with the example of allyl radicals.

Next we turn to the conjugated aryl-substituted methyl radicals (benzyl radicals). In all cases the geometries were optimized by the AM1 approach while the energies were evaluated by the ROHF and DFT methods. The ionization potential evaluated for the benzyl radical is presented in Table 6. Calculations by the ROHF, *ab initio* and hybrid DFT methods give results that have similar patterns to the ionization potentials calculated for aliphatic and allylic radicals. The ROHF underestimates the ionization potential by more than 1.4 eV. Clearly, for correct computing of the ionization potential, electron correlation is necessary. Even with moderate electronic correlation incorporated in BHandH DFT methods, considerable improvement in the ionization potential is obtained; however, the best ionization potential, employing the Becke3P86 hybrid (Table 6) is only 0.01 eV different from the experimentally determined value. Computing the ionization potential from the SOMO of the benzyl radical is, as for other radicals, not an acceptable approach. It has been a known and well documented fact that stability of benzyl radicals can be altered by positioning electron-donating or electron-withdrawing substituents on the aromatic ring.[25] To investigate the capability of hybrid DFT methods to compute ionization potentials for these systems we examined the *p*-methoxy- and *p*-cyano-benzyl radicals.

The results obtained are not in excellent agreement with the experimental values, as is the case with the plain benzyl radical. The computed ionization potential for the *p*-methoxybenzyl radical (Table 7) is 0.25 eV lower than the experimental value, indicating a weakness of Becke3P86 to generate very good ionization potentials. The computed ionization potentials with other methods studied here are as usual even worse. Using the SOMO energy for the computation of ionization potentials is proven also incorrect for the *p*-methoxybenzyl radical. For electron-deficient radicals, such as the *p*-cyanobenzyl radical, the predicted ionization value is now overestimated by 0.19 eV, when calculated with Becke3P86 (Table 8). The computed ionization potential with other methods are below the experimental data; this behaviour has been consistent throughout our study.

Table 8 Total energies (au) and ionization potentials (eV) for the *p*-methoxybenzyl radical calculated with AM1 generated geometry by using the 6-31 + G(d) basis set

Method	$E_{p\text{-methoxybenzyl radical}}$	$E_{p\text{-methoxybenzyl cation}}$	E_{SOMO}[a]	$E_{\text{i,a}}$[b]	$E_{\text{i,b}}$[c]
ROHF	−382.993 838 3	−382.786 762 3	−0.062 27	5.63	1.69
BHandH	−382.583 712 9	−382.349 819 6	−0.210 68	6.36	5.73
BHandHLYP	−385.212 114 6	−384.974 545 4	−0.215 57	6.46	5.87
Becke3LYP	−385.451 498 7	−385.215 685 6	−0.172 53	6.42	4.69
Becke3P86	−386.616 625 6	−386.358 167 8	−0.195 07	7.03	5.31
Exp.				6.84(10)	6.84(10)

[a] E_{SOMO} = total energy of the singly occupied molecular orbital. [b] $E_{\text{i,a}}$ = ionization potential calculated as the difference in energy of the methyl cation and methyl radical. [c] $E_{\text{i,b}}$ = ionization potential calculated from the SOMO.

Conclusions

The results presented here undoubtedly support hybrid DFT methods as a superior choice for calculating ionization potentials for conjugated radicals. Of the four studied hybrid DFT methods, Becke3P86 produces results that are closest to the experimental values. We demonstrated that it is not necessary to perform full optimization of the radical and corresponding cation with the BeckeP86 method to obtain quality results, since a single point Becke3LYP86 calculation on AM1 geometries produces almost identical results. This can be explained by the fact that the AM1 and DFT computed geometries are very similar. This approach should allow one to evaluate the ionization potential for large organic molecules that are of experimental interest. It has been demonstrated that this approach produces an ionization potential that is ± 0.2 eV different from experimentally determined values. Considering the large size of molecules studied and the precision of the computed results, we believe that this approach will find broad usage in organic chemistry.

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