J. Phys. Chem. A **1998,** *102,* 2609−2612 **2609**

Accuracy of G2 Calculations for the Reactions of Hydroxyl Radicals with Alkanes

Ignacio Aliagas and Scott Gronert*

Department of Chemistry and Biochemistry, San Francisco State University, San Francisco, California 94132

Received: October 21, 1997; In Final Form: January 28, 1998

Ab initio calculations at the G2 and G2(MP2) levels have been used to investigate the reactions of hydroxyl with methane, ethane, propane (2° position), and isobutane (3° position). Transition states were located, and activation energies as well as reaction enthalpies were computed. In general, the two computational methods give similar results. In terms of reaction enthalpies, the calculations underestimate them by about 1 kcal/mol. As for activation energies, an average error of ∼1 kcal/mol is observed; however, the ab initio results systematically overestimate the stabilizing effects of α-methyl substituents on the transition states. As a result, a fairly large error (3.2 kcal/mol) is found when comparing the barriers for methane and isobutane. The results suggest that G2 values be used with caution in these systems.

Introduction

In the troposphere, the reaction of an alkane with a hydroxyl radical is the first step in its oxidative decomposition.[1−3] The initially formed alkyl radical rapidly reacts with molecular oxygen to give a peroxy radical which can oxidize NO to NO_2 (Scheme 1). This shifts the atmospheric NO_x balance and therefore also has an effect on tropospheric ozone levels.

SCHEME 1

$$\mathrm{RH} \xrightarrow{\mathrm{HO}^\bullet} \mathrm{R}^\bullet$$

$$\mathrm{R}^\bullet \xrightarrow{\mathrm{O_2}} \mathrm{ROO}^\bullet$$

$$\mathrm{ROO}^\bullet \xrightarrow{\mathrm{NO}} \mathrm{RO}^\bullet + \mathrm{NO_2}$$

The resulting alkoxy radical can decompose via a number of pathways.[4] Given the importance of these atmospheric processes, it is no surprise that the reactions of hydroxyl radicals with alkanes have been the subject of numerous experimental studies in recent years.[5−14]

Although experiments have successfully determined the kinetics of a wide range of atmospheric processes, not all systems have proven amenable to experimental investigation due to the high reactivity or instability of the species involved. As a result, a reliable and accurate computational approach for studying atmospheric processes would be highly desirable. In recent years, Pople's G2 methodologies have emerged as powerful computational tools and have been applied to many systems with good success.[15−18] The G2 methods are based on the premise that improvement in the basis set and correlation treatment are additive and therefore can be dealt with in separate calculations. The combination of these calculations leads to a theoretical level that could not be reached (due to memory, disk, and time constraints) in a single calculation.

In this study, were have applied slight variations of the G2[15] and G2(MP2)[17] levels described by Pople. Each of the methods attempts to simulate calculations at the QCISD(T)/6-311+G-(3df,2p) level but uses slightly different approximations. The G2 calculations use the following additivity scheme:

$$\begin{aligned} E[\mathrm{G2}] = {} & E[\mathrm{MP4/6\text{-}311{+}G(d,p)}] + \\ & E[\mathrm{MP4/6\text{-}311{+}G(2df,p)}] + E[\mathrm{MP2/6\text{-}311{+}G(3df,2p)}] + \\ & E[\mathrm{MP2/6\text{-}311G(d,p)}]\ E[\mathrm{QCISD(T)/6\text{-}311G(d,p)}] - \\ & 2E[\mathrm{MP4/6\text{-}311G(d,p)}] - E[\mathrm{MP2/6\text{-}311{+}G(d,p)}] - \\ & E[\mathrm{MP2/6\text{-}311G(2df,p)}] + E(\mathrm{HLC}) + E(\mathrm{ZPVE}) \end{aligned} \qquad (1)$$

where E(HLC) represents an empirical correction and E(ZPVE) is the scaled zero-point vibrational energy (see below). The G2(MP2) method eliminates some of the more demanding calculations:

$$\begin{aligned} E[\mathrm{G2(MP2)}] = {} & E[\mathrm{QCISD(T)/6\text{-}311G(d,p)}] + \\ & E[\mathrm{MP2/6\text{-}311{+}G(3df,2p)}] - E[\mathrm{MP2/6\text{-}311G(d,p)}] + \\ & E(\mathrm{HLC}) + E(\mathrm{ZPVE}) \end{aligned} \qquad (2)$$

We have applied both computational schemes to the reactions of simple alkanes (methane, ethane, propane, and isobutane) with hydroxyl radicals. Transition states were located, and the barriers as well as the overall reaction enthalpies were calculated. An important advantage of these systems is that good experimental values are available for comparison. As a result, the accuracy and reliability of the computational methods can be assessed. It should be noted that in previous work Durant[19] has shown that the G2 method predicts transition-state energies with satisfactory results.

Methods

All calculations were completed with GAUSSIAN92[20] and GAUSSIAN94[21] using basis sets from the internal libraries. For the G2[15] and G2(MP2)[17] calculations, the standard procedures were followed with the following exceptions. The HF frequencies were calculated using the 6-31G(d,p) basis set on geometries optimized using the same basis set. In addition, the MP2 optimizations were completed with the 6-31G(d,p) basis set using the frozen core approximation. Test calculations indicate that these differences have only a modest effect on the computed G2 and G2(MP2) energies. In scaling the ZPVE, a factor of 0.9135 was used for HF zero-point energies and 0.9646 for MP2

---

* Corresponding author. E-mail gronerts@lewis.sfsu.edu.

S1089-5639(97)03390-2 CCC: $15.00

TABLE 1: Bond Dissociation Energies Calculated at 300 K[a]

	ΔH		ΔH(298 K)
$AH \rightarrow A^\bullet + H^\bullet$	G2	G2(MP2)	exp[b]
H_2	105.1	105.1	104.2
H_2O	118.8	119.3	119.3
methane	105.5	105.5	104.9
ethane	102.5	102.6	101.1
propane (2°)	99.8	99.9	98.6
isobutane (3°)	98.6	98.8	96.5
avg error[a]	0.9	1.1	
avg absolute error[a]	1.1	1.1	

[a] In kcal/mol. [b] References 23−25.

TABLE 2: Enthalpies for the Reactions of HO with Alkanes at 300 K[a]

	ΔH		ΔH(298 K)
$AH + HO^\bullet \rightarrow A^\bullet + H_2O$	G2	G2(MP2)	exp[b]
methane	−13.2	−13.9	−14.4
ethane	−16.3	−16.8	−18.2
propane (2°)	−19.0	−19.5	−20.7
isobutane (3°)	−20.1	−20.5	−22.8
avg error[a]	1.3	0.9	
avg absolute error[a]	1.3	0.9	

[a] In kcal/mol. [b] References 23−25.

zero-point energies.[22] Standard methods were used to generate thermal corrections.

Results and Discussion

Bond Strengths. One way to evaluate the accuracy of the theoretical methods is to test their ability to match known bond dissociation energies (BDE's). In many cases, experimental BDE's have been determined with small uncertainties, and these values provide excellent targets for the computational approaches.[23−25] In the present study, the BDE's of H_2, H_2O, methane, ethane, propane (2° position), and isobutane (3° position) have been calculated at the G2 and G2(MP2) levels of theory. The results are presented in Table 1. For this data set, the G2 and G2(MP2) values are very similar with the largest deviation between the methods being 0.5 kcal/mol for H_2O. The discrepancy found for H_2O arises from the almost zero contribution of the full correlation correction at the G2 level, which could be explained by the small basis set used for the QCISD(T) calculation. A similar situation has been found for anions[26] and could reflect a more general problem involving the oxygen lone pairs in H_2O and OH that could be better described by adding extra diffuse functions. At the G2(MP2) level this error is canceled out, leading to a bond dissociation energy closer to the experimental value.[27] Overall, the calculated values are in good agreement with experiment, and an average, absolute error of 1.1 kcal/mol is found for both the G2 and G2(MP2) methods. However, the calculated BDE's for the alkanes are systematically too large by about 1 kcal/mol. It should be noted that an exceptionally large error (>2 kcal/mol) is found for isobutane.

For the purposes of the present study, the enthalpy of hydrogen atom transfer to hydroxyl is also a useful measure of the quality of the calculation. In Table 2, enthalpies are listed for the hydrogen atom transfer reactions. Because G2(MP2) calculations predict stronger O−H bonds in H_2O (Table 1), more exothermic transfers (∼0.5 kcal/mol) are predicted than with the G2 method. The G2(MP2) values have the smallest errors, but they are consistently less exothermic than experiment. A disturbing aspect is that the deviations from experiment are not consistent and generally increase along the series methane (1.2 kcal/mol), ethane (1.9 kcal/mol), propane (1.7 kcal/mol), and isobutane (2.7 kcal/mol) for the G2 calculations. As a result, care must be taken in evaluating reactivity trends in the series.

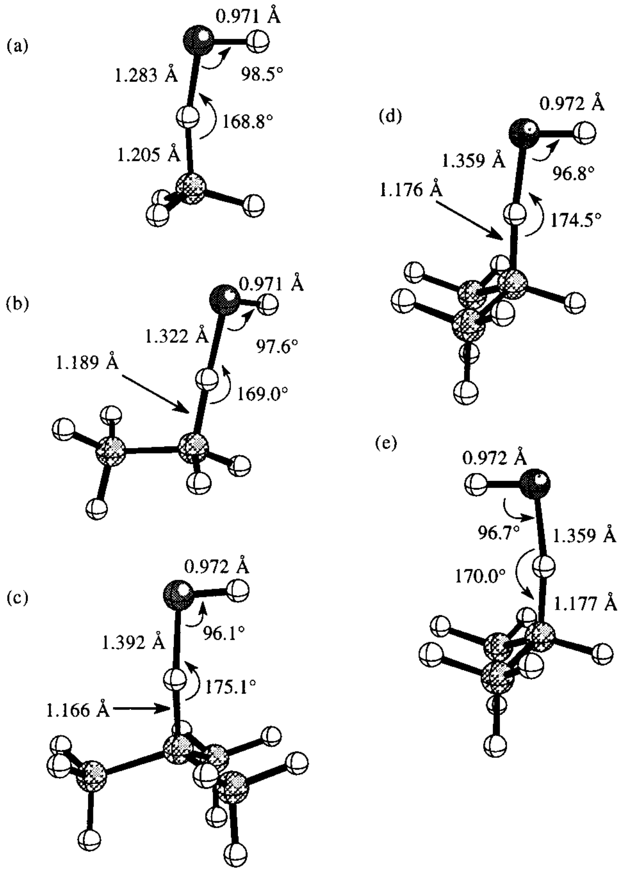

Figure 1. Transition states for the reaction of hydroxyl with (a) methane, (b) ethane, (c) isobutane, (d) propane (eclipsed), and (e) propane (staggered). Geometries at the MP2/6-31G(d,p) level.

Hydrogen Abstraction Transition States. Transition states for the reactions of hydroxyl with methane, ethane, propane (2° position), and isobutane (3° position) were located at the HF/6-31G(d,p) and MP2/6-31G(d,p) levels. The geometries are displayed in Figure 1. For methane, the Hartree−Fock and MP2 optimizations led to structures that were significantly different. Specifically, the MP2 calculations indicate the hydroxyl hydrogen prefers an eclipsing interaction with a methane hydrogen whereas HF indicates a staggered conformation. However, the difference in energy between these two conformations is trivial (<0.1 kcal/mol). For ethane and propane, an eclipsing interaction between the hydroxyl hydrogen and an α-hydrogen is also preferred. For example, two transition states were found for the reaction of hydroxyl with the secondary position of propane, but the transition state where the hydroxyl hydrogen eclipses the α-hydrogen (Figure 1d) is about 0.3 kcal/mol more stable than the one where it is staggered between the two methyl groups (Figure 1e). In the discussions to follow, only the most stable transition state is considered. For isobutane, a single transition state is found. Here, the hydroxyl hydrogen adopts a staggered conformation with respect to the methyl groups on the tertiary carbon.

As expected, the more exothermic reactions exhibit the earliest transition states. For example, the breaking C−H bond is shorter for isobutane (1.166 Å) than methane (1.205 Å). This effect is mirrored in the forming H−O bonds which are longer in the more exothermic reactions (1.392 Å in isobutane vs 1.283 Å in methane).

TABLE 3: Calculated Barriers for the Reactions of Alkanes with Hydroxyl[a]

	$\Delta H^{\ddagger}$	
alkane	G2	G2(MP2)
methane	5.9	5.9
ethane	2.9	3.0
propane (2°)	0.9	0.9
isobutane (3°)	−1.1	−1.0

[a] Values (in kcal/mol) calculated for 0 K.

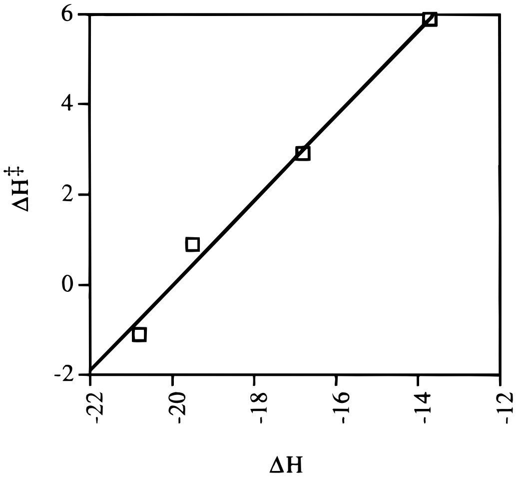

Figure 2. Plot of G2 activation enthalpies (0 K) vs G2 reaction enthalpies. Energies in kcal/mol. Slope = 0.94.

Hydrogen Abstraction Barriers. The G2 and G2(MP2) methods were used to calculate the enthalpic barriers to the above hydrogen abstraction reactions. The results are listed in Table 3. Because the eclipsed transition state for methane + hydroxyl is only found at the MP2 level, MP2 zero-point vibrational energies were used for this reaction. The values for the two methods (G2 and G2(MP2)) are virtually identical, and therefore nothing is gained in this system by going to the more demanding G2 protocol. The barriers smoothly decrease as one goes from the least (methane) to the most (isobutane) exothermic reaction. Surprisingly, the calculations predict that there is a *negative* enthalpy of activation for the reaction of hydroxyl with isobutane. This indicates that there may be a stable complex formed between the reactants before the transition state is reached. We have located this complex, and it is about 0.5 kcal/mol more stable than the separated reactants at the MP2/6-311+G(3df,2p) level (0 K).[28] Interestingly, the variation in activation enthalpy across the series (7 kcal/mol at G2, 0 K) is almost identical to the variation in reaction exothermicities (7.1 kcal/mol at G2, 0 K). A plot of $\Delta H^{\ddagger}$ vs ΔH is given in Figure 2. A linear relationship is observed ($r^2 = 0.988$) with a slope of 0.94. Consequently, almost all of the stabilizing effects of the α-methyl groups are realized in the hydrogen abstraction transition states despite the fact that they occur relatively early on the reaction coordinates (~15% extension of the C−H distance).

Comparing the ab initio barriers with those from experiment is not straightforward because tunneling as well as side reactions (e.g., removal of a primary hydrogen in isobutane) must be taken into account. In the past, several groups have used dynamics models of varying sophistication to link ab initio barriers to reaction kinetics in these systems.[5,29−35] These studies have shown that simple approaches fail, particularly in terms of estimating tunneling corrections.[5] Since the overall goal of this study is to test the ability of ab initio calculations to determine the energies of stationary points on the potential energy surface, we will forego a full dynamics treatment and instead rely on kinetic parameters derived from experiment. We have modeled the experimental data with an Arrhenius equation modified by a Wigner tunneling correction (3). The three free parameters in the equation are the Arrhenius factor (A), the activation energy (E_a), and the tunneling frequency ($\nu^{\ddagger}$) used in the Wigner correction (Γ). This approach is related to one taken by Martell et al. for modeling the reaction of hydroxyl with ethane but has a simplified preexponential.[5]

TABLE 4: Parameters Fit to Eq 3 for the Reactions of Alkanes with Hydroxyl[a,b]

alkane	A	$\nu^{\ddagger}$	E_a	E_a(G2)
methane	4.0	120	4.0	6.3
ethane	12.9	124	2.5	3.5
propane (2°)	5.4	128	1.3	1.1
isobutane (3°)	3.7	125	0.7	−0.2
avg error[a]				0.6
avg absolute error[a]				1.1

[a] Units: A, 10^{-12} cm^3/molecule; $\nu^{\ddagger}$, cm^{-1}; E_a, kcal/mol. [b] Data from refs 10, 12, 13, and 14. Temperatures used for fits range from ~230 to 430 K.

$$k = A\Gamma(\mathrm{T})e^{-E_a/RT} \qquad (3)$$

where $\Gamma(T) = 1 + (\mathrm{h}|\nu^{\ddagger}|^2/k_BT)/24$. Although the ab initio calculations give imaginary frequencies for the transition states, Martell et al. have shown that these values are significantly too large and overestimate the influence of tunneling.[5] Consequently, a more realistic fit is obtained by making $\nu^{\ddagger}$ a variable.

Modeling the reactions of hydroxyl with methane and ethane is straightforward because there is a single reaction pathway. We have used experimental data in the temperature range from ~230 to ~400 K to fit eq 3.[1,10,12] Table 4 lists the parameters obtained from a nonlinear, least-squares fit of the experimental data. The reactions of hydroxyl with propane and isobutane are complicated by the presence of two reaction channels. (Each of the hydrocarbons has two types of hydrogens.) To estimate partial rate data for the abstraction of a 2° hydrogen from propane and a 3° hydrogen from isobutane, we have taken advantage of Tully's studies on propane and isobutane where rate constants for the 2° and 3° centers were deduced from isotope effects.[13,14] For 2° hydrogens (i.e., propane), Tully recommends eq 4, and for the 3° hydrogens (i.e., isobutane), he recommends eq 5.

$$k^{\circ}_{\mathrm{sec}} = 7.76 \times 10^{-17} T^{1.61} e^{17.6/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}} \qquad (4)$$

$$k^{\circ}_{\mathrm{tert}} = 9.52 \times 10^{-14} T^{0.51} e^{-31.7/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}} \qquad (5)$$

Using these equations, data were generated at 30° intervals from 250 to 430 K. These data was then fit to eq 3. The parameters obtained from this fitting procedure also are listed in Table 4. In all cases, eq 3 gave good fits to the experimental data.

The A and E_a values listed in Table 4 differ from those in the literature because we have included the Wigner tunneling correction. For methane and ethane, this correction leads to E_a values that are slightly larger than those from a simple Arrhenius fit. However, for propane and isobutane, the E_a values are smaller than those taken directly from experiment because we have factored out the contribution from the abstraction of a primary hydrogen (a process with a high temperature dependence). Overall, the models give rational values. For example, the A values roughly correlate with the number of abstractable hydrogens (excluding methane), and the tunneling frequency is very similar for all the alkanes; however, it should be noted that the latter variable is not a particularly sensitive term in the fitting process.

To compare with experiment, we have converted our G2 $\Delta H^{\ddagger}$ values from 0 to 300 K and added 2*RT* to obtain E_a values at 300 K. The calculated E_a's are too large for methane and ethane and too small for propane and isobutane. The errors range from 0.2 kcal/mol for propane to 2.3 kcal/mol for methane. Overall, the average error (~1 kcal/mol) is within the expected accuracy range of the G2 method,[15] but errors of over 1 kcal/mol will limit the usefulness of the method for estimating reaction kinetics. The overall trend is that the calculations exaggerate the variation in barriers in going from methane to isobutane. The experimental variation in E_a values across the series is 3.3 kcal/mol, but G2 calculations lead to a variation of 6.5 kcal/mol. This is disappointing because it indicates that even high levels of theory cannot quantitatively characterize trends in reactivity and give accurate relative rates.[36]

Conclusions

The present work indicates that G2 and G2(MP2) calculations give similar results for the bond dissociation energies in methane, ethane, propane, and isobutane, but these values are from 0.6 to 2.5 kcal/mol larger than experiment. This leads to exothermicities that are too small for the reactions of these alkanes with hydroxyl. In this case, G2(MP2) is superior because it gives a better bond dissociation energy for H_2O.

When applied to the transition states of the hydrogen abstraction reactions, both methods give almost identical E_a values. The absolute errors in the E_a values are within the expected G2 accuracy range, but the calculations systematically overestimate the stabilizing effect of methyl substituents, and therefore fairly large errors are found for the relative activation energies (3.2 kcal/mol for methane vs isobutane). As a result, it appears that G2 values should be used with caution in efforts to predict the absolute or relative kinetics of hydrogen abstraction reactions. As an alternative, we are presently investigating density functional theory in these systems and the results will be reported in the near future.

References and Notes

(1) Atkinson, R. *Chem. Rev.* **1985**, *85*, 69.
(2) Atkinson, R. *Atmos. Environ.* **1990**, *24A*, 1.
(3) Carter, W. P. L.; Atkinson, R. *J. Atmos. Chem.* **1985**, *3*, 377.
(4) Atkinson, R.; Carter, W. P. L. *J. Atmos. Chem.* **1991**, *13*, 195.
(5) Martell, J. M.; Mehta, A. K.; Pacey, P. D.; Boyd, R. J. *J. Phys. Chem.* **1995**, *99*, 8661.
(6) Mellouki, A.; Téton, S.; Laverdet, G.; Quilgars, A.; Le Bras, G. *J. Chim. Phys.* **1994**, *91*, 473.
(7) Atkinson, R. *Int. J. Chem. Kinet.* **1987**, *19*, 799.
(8) DeMore, W. B. *Geophys. Res. Lett.* **1992**, *19*, 1367.
(9) Finlayson-Pitts, B. J.; Ezell, M. J.; Jayaweera, T. M.; Berko, H. N.; Lai, C. C. *Geophys. Res. Lett.* **1992**, *19*, 1371.
(10) Talukdar, R. K.; Mellouki, A.; Gierczak, T.; Barone, S.; Chiang, S.-Y.; Ravinshankara, A. R. *Int. J. Chem. Kinet.* **1994**, *26*, 973.
(11) Tully, F. P.; Droege, A. T.; Koszykowski, M. L.; Melius, C. F. *J. Phys. Chem.* **1986**, *90*, 691.
(12) Vaghjiani, G. L.; Raishankara, A. R. *Nature* **1991**, *350*, 406.
(13) Tully, F. P.; Goldsmith, J. E. M.; Droege, A. T. *J. Phys. Chem.* **1986**, *90*, 5932.
(14) Droege, A. T.; Tully, F. P. *J. Phys. Chem.* **1986**, *90*, 1949.
(15) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.
(16) Curtiss, L. A.; Carpenter, J. E.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1992**, *96*, 9030.
(17) Curtiss, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 1293.
(18) Pople, J. A.; Head-Gordon, M.; Fox, D. J.; Raghavachari, K.; Curtiss, L. A. *J. Chem. Phys.* **1989**, *90*, 5622.
(19) Durant, J. L., Jr.; McMichael-Rohlfing, C. *J. Chem. Phys.* **1993**, *98*, 8031.
(20) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92*; Revision C ed.; Gaussian, Inc.: Pittsburgh, PA, 1992.
(21) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; W. Gill, P. M.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*; Revision B.3 ed.; Pittsburgh, PA, 1995.
(22) Pople, I. A.; Scott, A. P.; Wong, M. W.; Radom, L. *Isr. J. Chem.* **1993**, *33*, 345.
(23) Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744.
(24) Ruscic, B.; Berkowitz, J.; Curtiss, L. A.; Pople, J. A. *J. Chem. Phys.* **1989**, *91*, 114.
(25) Seakins, P. W.; Pilling, M. J.; Niiranen, J. T.; Gutman, D.; Krasnoperov, L. N. *J. Phys. Chem.* **1992**, *96*, 9847.
(26) Gronert, S. *Chem. Phys. Lett.* **1996**, *252*, 415.
(27) Another problem is that the energies do not converge quickly (as a function of theoretical level) for water and hydroxyl. As a result, each of the calculations that go into the G2 approximation gives a very different BDE (±4 kcal/mol), and therefore, it is not surprising that the additivity schemes break down.
(28) The complex is more stable than the transition state on the electronic potential energy surface but less stable when zero-point energies are included. This suggests virtually no barrier to the hydrogen atom transfer..
(29) Melissas, V. S.; Truhlar, D. G. *J. Phys. Chem.* **1994**, *98*, 875.
(30) Melissas, V. S.; Truhlar, D. G. *J. Chem. Phys* **1993**, *99*, 1013.
(31) Truong, T. N.; Truhlar, D. G. *J. Chem. Phys.* **1990**, *93*, 1761.
(32) Gonzalez, C.; McDouall, J. J. W.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 7467.
(33) Nyman, G.; Clary, D. C. *J. Chem. Phys.* **1994**, *101*.
(34) Nyman, G. *Chem. Phys. Lett.* **1995**, *240*, 571.
(35) Dobbs, K. D.; Dixon, D. A. *J. Chem. Phys.* **1993**, *98*, 8852.
(36) Spin contamination is minor in these systems and is probably not the key to the poor values. Also, test optimizations at the ROMP2 level gave similar geometries.