

- Levenspiel, O. (1999). *Chemical Reaction Engineering*, 3rd ed., New York, John Wiley, p. 326.
- Liatis, Th. S. (1983). A review on the exploitation of flying ash. In: *Proceedings of the Meeting on the Exploitation of Flying Ash-Pollution Problems in Lignite Thermolectric Stations, Public Power Corporation of Greece, Ptolemais Greece*, April 15–16, pp. 1–13 [in Greek].
- Méndez-Vigo, I. and Pisa, J. (1998). The Puertolano IGCC plant: Pre-operational records and demonstration targets, in *Gasification—The Gateway to a Cleaner Future, Proceedings of the 3rd European Conference on Gasification, Dresden, Germany*, London Institution of Chemical Engineers.
- Mueller, R. and Karg, J. (1987). Assessment of coal gasification systems for combined cycle power plants, paper presented at the ASME/IEEE Power Generation Conference, Miami Beach, Florida, Oct. 4–8.
- Rost, M., Van Heek, K. H., and Knob, K. (1988). Low pollutive power generation by allothermal coal gasification using the MBG process; *VGB Kraftwerkstechnik* **68**(5), 416–424.
- Salmas, C. E., Tsetsekou, A. H., Hatzilyberis, K. S., and Androutsopoulos, G. P. (2001). Lignite meso-pore structure evolution during drying: Effect of temperature and heating time, *Drying Technol.*, **19**, 35–64.
- Schilling, H. D., Bonn, B., and Krauss, U. (1981). *Coal Gasification*, 2nd ed., Norell, Mass., Graham & Tortman.
- Theoflou, N. (1997). Gasification of solid fuels: Experience from the gasification of Greek lignite. *Technica Chronica*, **2**, 38–44 [in Greek].
- Zero Emission Coal Alliance. (2000). Technology promises emission-free electric power from coal, *Pollution on Line*, Aug. 17, www.pollutiononline.com/content/news/article.asp?DocID={07E80835-7461-11D4-8C58-009027DE0829}

ASSESSMENT OF THE SUITABILITY OF USING THE COMPOSITE G2, G3, AND CBS-RAD METHODS FOR PREDICTING ACTIVATION ENERGIES

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In this work, the accuracy of the G2, G3, and CBS-RAD methods for predicting activation barriers of ligand transfer reactions is investigated. We find that the zero point corrected G2 method has an RMS error of 3.82 kcal/mol for activation barriers. The G3 method has an RMS error of 4.16 kcal/mol. After adding thermal corrections to the G2 and zero point corrected results, the RMS error for the G2 method is 4.92 kcal/mol, while the error for the G3 method is 4.55 kcal/mol. In contrast, the CBS-RAD method has errors of 3.80 kcal/mol for zero point energy corrected activation energies, and 2.82 kcal/mol for thermally corrected results. The G3 method was found to require only 40% of the computational time required for the G2 method, making it an attractive alternative for predicting activation energies yielding errors of about 4 kcal/mol. The CBS-RAD method has a computational cost four times greater than that of the G2 method and gives an improvement of only about 1 kcal/mol.

Keywords: Gaussian; Ab initio; CBS; Activation energy; Thermal corrections

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INTRODUCTION

Ab initio calculations have been used for many years to find thermodynamic properties that have been difficult to measure experimentally. And, as computational power increases, so has the accuracy of the methods used to find the energies of different systems. The G2 method of Pople and coworkers has proven to be extremely accurate in predicting heats of reaction, heats of formation, and ionization potentials (Curtiss et al., 1991, 1997a; Bauschlicher and Partridge, 1995; Blowers et al., 1998; Lee and Masel, 1996).

However, the G2 method is extremely expensive for larger molecules of interest due to the large basis sets and computational methods used. Pople and others have done much work to develop reduced basis set methods like the G2(MP2) methods (Curtiss et al., 1993a, 1996; Nicolaides et al., 1996; Smith and Radom, 1994, 1996; Mebel et al., 1995). The main thrust behind their work is to reduce the computational demand of the calculations by using smaller basis sets for some calculation steps while still giving accurate answers. Similarly, the more recent G3 method has shown great promise for predicting heats of reaction, ionization potentials, and other phenomena (Curtiss et al., 1995, 1997b, 1998; Baboul et al., 1999; Kedziora et al., 1999) at a reduced cost. This method is computationally much cheaper than the G2 method, yet still yields very accurate results for these thermodynamic properties.

More recently, another series of composite energy methods called the complete basis set methods have been developed (Peterson et al., 1988, 1991; Peterson and Allaham, 1991; Montgomery et al., 1994, 1999, 2000; Ochterski et al., 1996; Morihovitis et al., 1999; Mayer et al., 1998). These methods eliminate some of the empirical correlations that have been included in the Gaussian-n series of methods while still giving very accurate heats of formation and enthalpies of reaction.

All of these composite energy methods were developed for stable species like reactants, products, ions, and radicals, but were not developed to address the issues specific to transition states. Despite the fact that these methods were not developed to handle transition state energies, many researchers have extrapolated their use to find activation energies for reactions (Kondo et al., 2000; So, 1999; Caralp et al., 1999; Korchowiec et al., 1999; Jodkowski et al., 1998; Berry et al., 1998; Hand et al., 1998; Bettinger et al., 2000; Feller et al., 2000; Chen and Bozzelli, 2000a, 2000b; Jursic, 2000a, 2000b; Zhang, et al., 2000).

In previous work, our interest has been in calculating activation barriers and the physical interactions that lead to them (Blowers and Masel, 1999a, 2000; Blowers et al., 1998). For this work to be successful, it is necessary to use the composite G2, G3, and complete basis sets (CBS) methods to find accurate activation energies. However, no cross-reaction

study has yet been done to see if these methods are capable of reproducing experimental activation energies even though many researchers have been using them for this application.

In this article, activation barriers for 17 ligand transfer reactions have been calculated at the G2, G3, and CBS-RAD levels. After comparing the calculated zero point energy results and thermally corrected results to experimental values, it can be shown that both the G2 and G3 methods yield experimental activation energies with RMS (root-mean-square) errors of about 4 kcal/mol. The CBS-RAD method gives the lowest errors when thermal corrections are included. For all methods, maximum errors of about 10 kcal/mol were found.

COMPUTATIONAL METHODS

All calculations in this work were done using the Gaussian 92 (1993), Gaussian 94 (1995), and Gaussian 98 (1998) programs. Geometries were optimized at the MP2(full)/6-31g* level of calculation, as suggested by Pople and others for the G2 and G3 calculations (Curtiss et al., 1991, 1993b, 1998; Pople et al., 1989). For the CBS-RAD method, QCISD(fc)/6-31g* (Mayer et al., 1998) optimizations were done. A comparison of the calculations needed for each method is shown in Table I. All products and reactants were verified to be stable structures with frequency calculations, while all transition states were found to be first-order saddle points with only one negative eigenvalue. Furthermore, potential energy surfaces were developed for each reaction to show that the transition state and intrinsic reaction coordinate linked the correct products with reactants.

For some of the reactions, the G3/B3LYP (Curtiss et al., 1997a) method was also used to estimate the activation energy. This method involves optimizations at the B3LYP/6-31g* level with higher level calculations following the G3 method. This method was chosen because B3LYP geometries are considered to be slightly superior to MP2/6-31g* level calculations for some species (Bauschlicher, 1995; Stephens et al., 1994).

Also, some calculations were done with the G2(+) method of Glukhovtsev et al. (1995a, 1995b, 1996a, 1996b), which utilizes geometry optimizations at the MP2(fc)/6-31 + g* level followed by higher level G2 calculations. This method has been used in some anionic and cationic reactions where it gave superior results to the standard G2 calculation using the MP2(full)/6-31g* geometry.

RESULTS AND DISCUSSION

Bimolecular ligand transfer reactions were chosen for this work because extensive research on the origins of activation barriers for this class of

reactions had already been completed (Blowers and Masel, 1999a, 2000; Blowers et al., 1998). The 17 specific reactions from this class were chosen because of:

1. their relatively accurate rate constants and activation energies from experimental data;
2. their relatively small size and their ability to be handled with the computationally demanding CBS-RAD method;
3. the ability to use a standardized method for thermal corrections for a single class of reactions; and
4. the 17 reactions show a wide range of activation energies, between 2 and 35 kcal/mol.

Several sources of experimental data were used for the reactions in this work. Originally, activation energies were taken from Westley's compendium of combustion data (Westley, 1980). This is the source of most data in the National Institute of Standards and Technology (NIST) database; however, several of the data points in Westley are estimated parameters from kinetic models and had not been experimentally measured when the database was published. To address this issue, experimental measurements for the reactions estimated in Westley were taken from several other data compendia (Bamford and Tipper, 1976; Baulch et al., 1994; Hucknall, 1985; Gardiner, 1984).

In general, experimental error estimates of the rate constants for the reactions in this study are plus or minus 0.5 in the log-k domain. Additionally, error estimates for the activation energies are between 1-10%. Table II shows a comparison of the composite activation energy results with the available experimental values. The table also shows E_0 energies with thermal corrections that were found with the standard equation:

$$E_{act}(T) = E_0 + \Delta\Delta H^*(T) + 2RT \quad (1)$$

for bimolecular reactions (Wong and Radom, 1998). In this equation, E_0 is the zero point corrected energy from the calculational method at 0°C, R is the ideal gas constant, and $\Delta\Delta H^*(T)$ is the thermal correction to the enthalpy from the frequency calculation at the geometry optimization level. In this work, temperatures within the experimental range for each reaction were selected for the thermal correction calculations.

Figure 1 shows a plot of the calculated E_0 energies versus the experimental activation energy while Figure 2 shows a plot of the thermally corrected activation energies versus the experimental values. The plots show that the data from the methods are in close agreement with the experimental data. The G2 E_0 energy has an RMS error of 3.82 kcal/mol,

Table I Brief Description of the Composite Energy Methods Used in This Work

Method	Geometry optimization	Single-point calculations	Frequency	Empirical corrections
G2	MP2(full)/6-31g*	MP4SDTQ(fc)/6-311g**	MP2(full)/6-31g*	Higher level corrections
	MP4SDTQ(fc)/6-311g**	MP4SDTQ(fc)/6-311g(2df,p)	MP2(fc)/6-311 + g(3df,2p)	Scale ZPE
G3	MP2(full)/6-31g*	MP4SDTQ(fc)/6-31g*	MP2(full)/big basis	Higher level corrections
	MP4SDTQ(fc)/6-31g*	MP4SDTQ(fc)/6-31 + g*	QCISD(T)/6-31g*	Scale ZPE
CBS-RAD	QCISD(fc)/6-31g*	CCSD(T)(fc)/6-31 + g*	MP2(fc)/CBSB3	
		MP4SDQ(fc)/CBSB4	MP4SDQ(fc)/CBSB4	

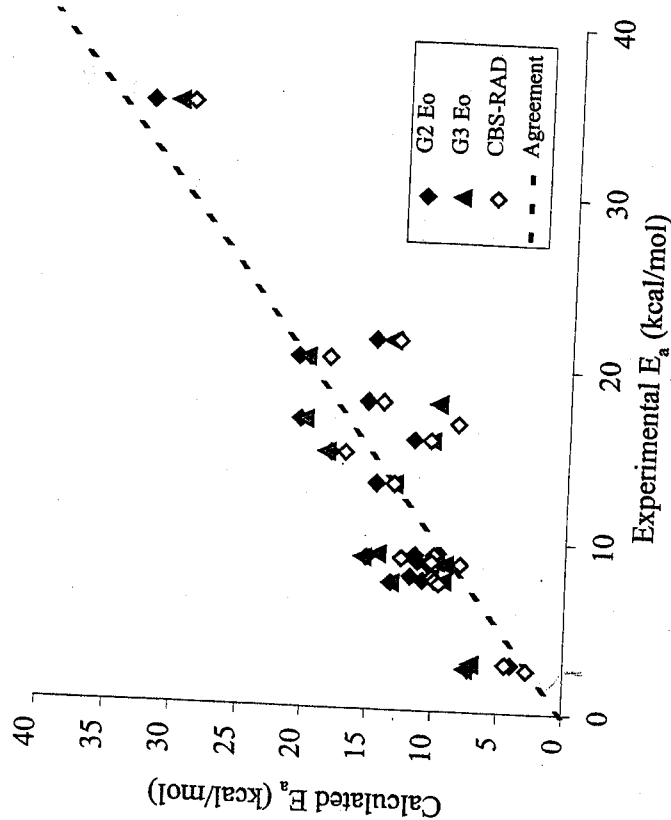


Figure 1. A comparison of the zero point corrected E_0 , G2, G3, and CBS-RAD energies compared to experimental activation energies. All energies are in kcal/mol and the dashed line indicates perfect agreement between the calculational and experimental results.

while the G3 E_0 energy has an RMS error of 4.16 kcal/mol and the CBS-RAD method shows an error of 3.80 kcal/mol. Maximum errors, on the other hand, are 6.5 kcal/mol for the G2 E_0 energy for the $H + NH_3$ reaction and 7.9 kcal/mol for the G3 E_0 energy for $CH_3 + CH_3CH_3$. The maximum error for the CBS-RAD method is 8.2 kcal/mol for the $H + NH_3$ reaction. A summary of the error information is shown in Table III.

The data in Table II and information in Table III exhibit a few trends for the E_0 energies compared to the experimental results. First, all methods slightly overestimate activation energies for this data set. Only four reactions are underpredicted by these methods, with larger errors than the overprediction errors. This is also seen in Figure 1 where most of the data lies above the parity line. Second, all but three of the reactions in this set are within 5 kcal/mol of the experimental result for the G2 method. With the G3 method, six of the reactions are more than 5 kcal/mol away from the experimental result. Only four of the reactions are off by more than 5 kcal/mol with the CBS-RAD method. It is possible that

Note: For multichannel reactions, only terminal hydrogen abstractions from the end-carbon were calculated in this work. It is not clear from experimental data which hydrogen atoms were removed. All energies are in kcal/mol.

^aHucknall, 1985.
^bWestley, 1980.
^cBamford and Tipper, 1976.
^dBaulch, 1994

Reaction	Exp. Temp. Kelvin	G2 E_0	G2 + thermal correction	G3 E_0	G3 + thermal correction	CBS-RAD + thermal corr.
$H + CH_3CH_2 \rightarrow H_2 + CH_2CH_3$	281	11.50	11.50	14.31	14.31	10.05
$H + CH_3CH_2 \rightarrow H_2 + CH_2CH_3$	281	11.82	12.46	10.27	10.92	10.09
$H + CH_3CH_2 \rightarrow H_2 + CH_2CH_3$	883	11.26	14.50	9.85	13.09	12.53
$H + CH_3CH_2NH_2 \rightarrow H_2 + CH_2CH_2NH_2$	8.70 ^b					
$H + CH_3OH \rightarrow H_2 + CH_2OH$	8.60 ^b	10.51	10.75	9.21	9.45	8.10
$H + H \rightarrow H_2 + H$	7.60 ^b	10.88	12.53	9.31	10.96	11.23
$H + CH_3 \rightarrow H_2 + CH_3$	13.16 ^a	14.60	16.04	13.23	14.67	14.50
$H + CH_4 \rightarrow H_2 + CH_4$	640	14.60	16.04	13.23	14.67	14.50
$H + NH_3 \rightarrow H_2 + NH_3$	1500	14.96	19.63	13.70	18.37	17.55
$H + H_2O \rightarrow H_2 + OH$	20.36 ^a	20.86	20.79	20.25	20.17	18.07
$H + CH_3CH_2OH \rightarrow H_2 + CH_3CHOH$	15.79 ^c	11.79	14.05	10.45	12.71	12.63
$H + HF \rightarrow H_2 + F$	3700	32.51	46.72	30.60	44.81	43.21
$H + HF \rightarrow H_2 + F$	473	18.18	18.51	18.49	18.83	17.42
$CH_3 + CH_4 \rightarrow CH_4 + CH_3$	14.90 ^b	18.18	18.51	18.49	18.83	17.07
$CH_3 + CH_4 \rightarrow CH_4 + CH_3$	298	7.23	5.73	7.47	5.96	2.77
$OH + CH_4 \rightarrow H_2O + CH_3$	7.41 ^a	13.29	11.47	13.28	11.46	9.63
$O + CH_4 \rightarrow OH + CH_3$	16.79 ^a	20.58	25.88	20.27	25.57	8.52
$H + O_2 \rightarrow OH + O$	300	20.58	25.88	20.27	25.57	15.11
$O + NH_3 \rightarrow OH + NH_2$	8.88 ^a	15.24	14.28	15.47	14.51	10.36
$OH + CH_3 \rightarrow H_2O + CH_2$	2.78 ^c	4.03	3.23	7.04	6.24	3.55
$CH_3 + CH_3CH_3 \rightarrow CH_4 + CH_3$	11.75 ^d	15.44	18.06	10.02	12.63	14.82

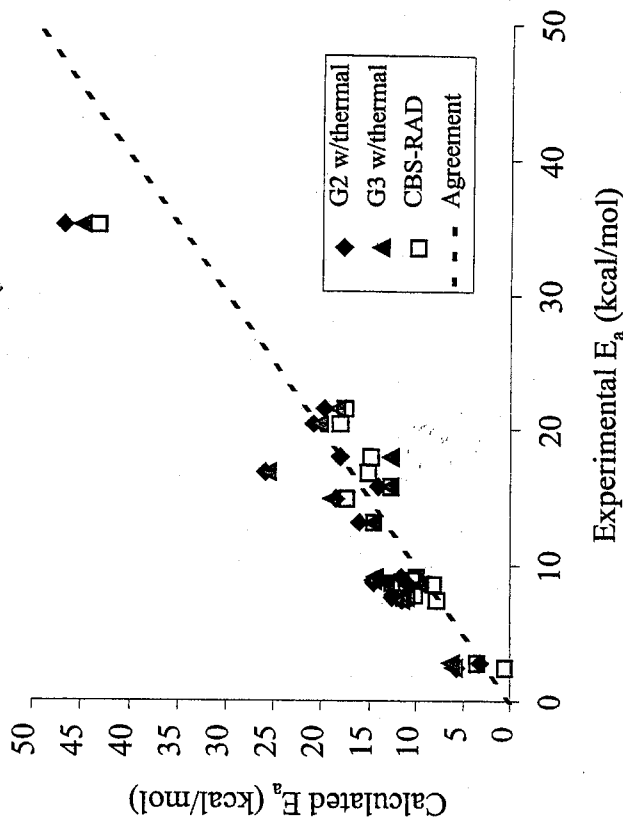


Figure 2. A comparison of the thermally corrected G2, G3, and CBS-RAD energies compared to experimental activation energies. All energies are in kcal/mol and the dashed line indicates perfect agreement between the calculational and experimental results.

these deviations for the composite energy methods are attributable to the omission of thermal corrections to the calculated energies.

By adding thermal corrections to the 0 K barrier heights, the RMS error for the G2 method now becomes 4.92 kcal/mol. For the G3 method, the RMS error goes up only 0.39 kcal/mol to 4.55 kcal/mol. Errors for the CBS-RAD method decrease by 1 kcal/mol once the ther-

Table III Comparison of the Errors of Several Computational Methods for Predicting Activation Energies Compared to Experimental Results

Method\energy	RMS	Maximum error
G2	3.82	- 6.54
G2 w/thermal	4.92	+ 11.72
G3	4.16	- 7.90
G3 w/thermal	4.55	+ 9.81
CBS-RAD	3.80	- 8.31
CBS-RAD w/thermal	2.82	+ 8.21

All values are in kcal/mol.

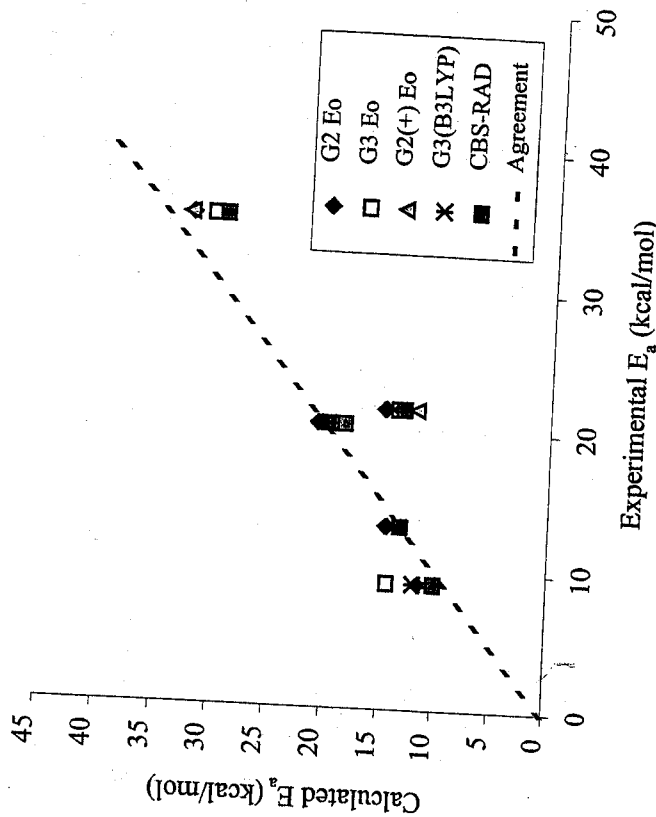


Figure 3. A comparison of the zero point corrected E_0 energies for several calculational methods compared to the experimental results. All energies are in kcal/mol and the dashed line indicates perfect agreement between the calculational and experimental results.

mal corrections are added. Figure 2 shows that at least two of the reactions have thermal corrections that are too large, shifting the predicted results to the opposite side of the parity line. This phenomenon is caused in part by the low level of calculational method used for the vibrational analysis. Using a higher level of calculational method used for the vibrational analysis may lead to improved thermal corrections. The H + O₂ reaction has errors of about 9 kcal/mol for the G2 and G3 methods after the thermal corrections are added. And the reaction of H + HF has errors of 11 kcal/mol for the G2 thermally corrected energy and 10 kcal/mol for the G3 thermally corrected results.

After adding the thermal corrections, four of the reactions are more than 5 kcal/mol away from the experimental results for the G2 method. For the G3 method, five of the reactions are still 5 kcal/mol away from the experimental results. The CBS-RAD method has only one reaction that is now more than 5 kcal/mol away from the experimental results. Clearly, some effects must be leading to the poor performance of the G2 and G3 composite methods for predicting activation energies once thermal corrections are included. Again, this was expected since the

composite energy methods were never developed to handle transition states and activation energies.

One possibility that may be causing the discrepancy between the calculated results and experimental results could be the effect of tunneling on lowering the observed barrier height. The calculations performed in this work do not include tunneling effects on the observed activation energies. Other researchers have found that tunneling can lower the effective barrier height by as much as 10 kcal/mol for similar systems (Truong, 1994; Espinosa-Garcia et al., 1997; Hand et al., 1998; Blowers and Masel, 1999b). We are currently evaluating the effect of tunneling on the barrier height, and this information will appear in a future publication.

Another possibility is that the MP2(full)/6-31g* geometry may not be the best choice of calculational method for transition state structures. Glukhovtsev et al. (1995a, 1995b, 1996a, 1996b) have found that the MP2(fc)/6-31 + g* geometry leads to better description of transition state structures for ionic reaction systems. Calculations were done using this geometry optimization and the G2 method for a few select cases. This method has been designated the G2(+) method and the results for the zero point corrected E_0 energies are shown in Table IV. The reactions in Table IV were chosen because other extensive calculations have already been completed for this set of reactions (Blowers and Masel, 1999b).

Calculations were also done using the B3LYP/6-31g* optimized geometry, which researchers have found to give better results (Baboul et al., 1999; Pople et al., 1989; Curtiss et al., 1993b) in some cases. This geometry was combined with the G3 method to give the G3(B3LYP) (Baboul et al., 1999) results, which are also shown in Table IV. A comparison of all E_0 energies versus the experimental energies is shown in Figure 4.

Figure 3 shows that the G2(+) zero point corrected results do not differ greatly from the other composite energy results. Likewise, the B3LYP geometry using the G3 method appears to give similar agreement

Table IV Comparison of Several Computational Methods for Predicting Activation Energies Without Thermal Corrections

Reaction	Method					
	Expt	G2	G3	CBS-RAD	B3LYP/G3	G2(+)
H + HF → H ₂ + F	35.00	32.51	30.60	29.54	no TS	32.73
H + H ₂ O → H ₂ + OH	20.36	20.86	20.25	18.53	19.90	20.04
H + CH ₄ → H ₂ + CH ₃	13.16	14.60	13.23	13.23	13.79	13.39
H + NH ₃ → H ₂ + NH ₂	21.50	14.96	13.70	13.18	14.17	12.01
H + CH ₃ CH ₃ → H ₂ + CH ₂ CH ₃	9.11	11.50	14.31	10.05	11.92	10.61

All energies are in kcal/mol.

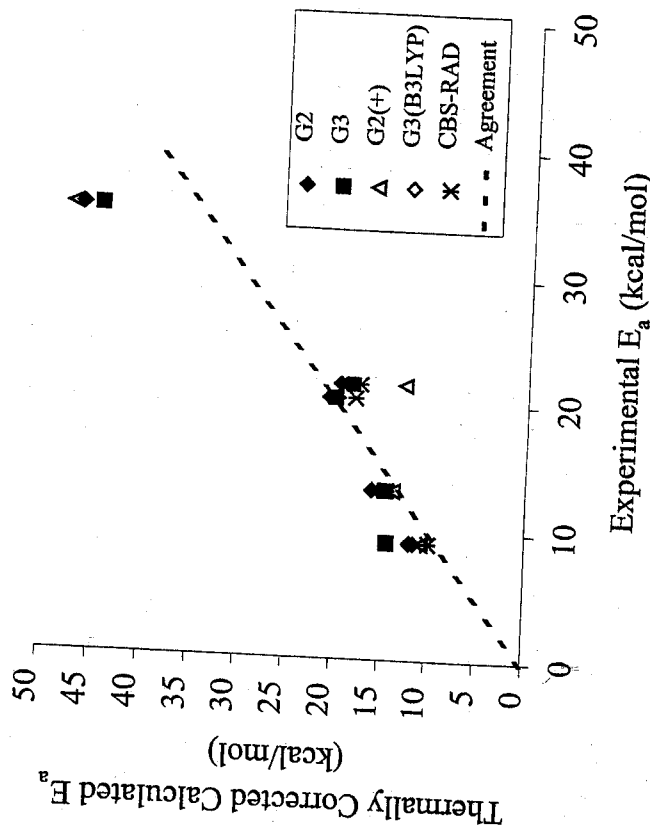


Figure 4. A comparison of the thermally corrected energies for several calculational methods compared to the experimental results. All energies are in kcal/mol and the dashed line indicates perfect agreement between the calculational and experimental results.

with the experimental results, even without zero point corrections. However, the H + HF reaction has no barrier using this calculational level (Montgomery et al., 1999). This is a critical failure of the B3LYP/6-31g* calculation for this reaction. According to the G3(B3LYP) method, this reaction would have an activation energy of zero compared to the experimentally observed 35 kcal/mol.

Table V Comparison of Activation Energies for Several Methods Including the Thermal Corrections

Reaction	Method					
	Expt	G2	G3	CBS-RAD	B3LYP/G3	G2(+)
H + HF → H ₂ + F	35.00	46.72	44.81	43.21	no TS	47.58
H + H ₂ O → H ₂ + OH	20.36	20.79	20.17	18.07	19.92	20.14
H + CH ₄ → H ₂ + CH ₃	13.16	16.04	14.67	14.50	15.25	13.80
H + NH ₃ → H ₂ + NH ₂	21.50	19.63	18.37	17.55	18.95	12.80
H + CH ₃ CH ₃ → H ₂ + CH ₂ CH ₃	9.11	11.50	14.31	9.89	11.96	10.67

All energies are in kcal/mol.

Thermal corrections were added to the G2(+) and G3(B3LYP) E_0 energies using the appropriate results from the frequency calculations. Table V and Figure 4 show that the H + HF reaction has thermal corrections that are routinely overestimated by all methods. On the other hand, thermal corrections for the H + NH₃ reaction are well represented with all levels of calculation except for the MP2(fc)/6-31 + g* level.

Now that we have seen that the geometry optimization level does not significantly improve activation energy estimates, a final cause for the discrepancy between the calculated G2 and G3 results and the experimental results may be that the higher level corrections of the G2 and G3 methods have been optimized for stable products and reactants. The higher level correction (HLC) parameters could be reoptimized for both Gaussian methods to improve agreement with the experimental activation energies. There is some justification for taking this approach since the G3 method requires different HLC parameters for atoms than it does for molecules (Curtiss et al., 1995). In fact, transition states could be another separate class of species with their own parameters.

Table VI shows the root mean squared errors of each method for predicting activation energies compared to the experimental results when the HLC parameters are optimized for the transition states. We find that the values can be optimized for each method, leading to improvements of between 0.5 and 1 kcal/mol for RMS values. However, it is not possible to eliminate the errors by optimizing these empirical parameters.

We have seen from these results that both of the G2 and G3 results have RMS errors of about 4 kcal/mol. Maximum errors are larger for the G3 method than they are for the G2 method by about 3 kcal/mol. However, the G3 method has slightly lower RMS errors than the G2

Table VI Summary of Activation Energy Results After Optimizing the Higher Level Correction Parameters for Transition States

Method	Parameter		E_a RMS error (kcal/mol)
	a	b	
G2	Starting E_0 values	-0.19	3.82
	Optimized E_0 values	-0.57	3.30
	Starting thermal values	-0.19	4.92
	Optimized thermal values	-0.19	3.72
G3	Starting E_0 values	-6.386	4.16
	Optimized E_0 values	-7.047	3.67
	Starting thermal values	-6.386	4.55
	Optimized thermal values	-6.723	3.75

method once thermal corrections to the barrier height are added. Regardless, both methods tend to overpredict activation barriers either with or without thermal corrections to the 0 K barrier height. The CBS-RAD method has the lowest error after thermal corrections have been included, with an error of 2.82 kcal/mol. Also, the CBS-RAD method performs better on a larger number of reactions than the other composite energy methods.

The computational demands of the G2 and G3 methods are quite different. The newer G3 method requires less computational time due to the smaller basis sets used in the calculations. For example, a comparison of the G2 and G3 methods for computing the energy of trifluoropropane using the Gaussian 98 (1998) program on the Exemplar NCSA super-computer shows that the G2 method required 105.5 h of CPU time, while the G3 method required only 40.9 h. This is a savings of 61% on CPU time without much loss in accuracy for predicting activation energies and heats of reaction. On the other hand, the CBS-RAD method requires 422.0 hours of CPU time on the same system. The increase in accuracy of activation energies from the CBS-RAD method does not seem to justify the additional 400% increase in CPU time over the G2 method. Due to the computational savings and relative accuracy of the results, the G3 method is recommended for evaluating activation energies for ligand transfer reactions.

CONCLUSIONS

In this work, the G2 and G3 methods predict activation energies with RMS errors of 3.82 and 4.16 kcal/mol, respectively. The CBS-RAD method has an error of 3.80 kcal/mol. After adding thermal corrections to the 0 K barrier heights, the RMS errors become slightly worse with values of 4.92 and 4.55 kcal/mol for the G2 and G3 methods, but decrease by 1 kcal/mol for the CBS-RAD results. The maximum deviations in this work are 11.72 and 9.81 kcal/mol for the G2 and G3 methods, respectively, while the CBS-RAD method has a maximum error of 8.21 kcal/mol. Qualitatively, the CBS-RAD method comes closest to the experimental activation errors for more reactions than the other two methods, with only one reaction being off by more than 5 kcal/mol. However, because all three composite methods lead to very similar results for most of the cases studied here, the G3 method is recommended due to its reduced computational demands.

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REFERENCES

- Baboul, A. G., Curtiss, L. A., Redfern, P. C., and Raghavachari, K. (1999). *J. Chem. Phys.*, **110**, 7650.
- Bamford, C. H. and Tipper, C. F. H. (1976). *Comprehensive Chemical Kinetics*, vol. 18, Elsevier, New York.
- Baulch, D. L., Cobos, C. J., Cox, R. A., Frank, P., Hayman, G., Just, T., Kerr, J. A., Murrells, T., Pilling, M. J., Troe, J., Walker, R. W., and Warnatz, J. (1994). *J. Phys. Chem. Ref. Data*, **23**, 847.
- Bauschlicher, C. W. (1995). *Chem. Phys. Lett.*, **246**, 40.
- Bauschlicher, C. W. and Partridge, H. (1995). *J. Chem. Phys.*, **103**, 1788.
- Berry, R. J., Yuan, J., Misra, A., and Marshall, P. (1998). *J. Phys. Chem. A*, **102**, 5182.
- Bettinger, H. F., Schleyer, P. V., Schaefer, H. F., Schreiner, P. R., Kaiser, R. I., and Lee, Y. T. (2000). *J. Chem. Phys.*, **113**, 4250.
- Blowers, P. and Masel, R. I. (1999a). *J. Phys. Chem. A*, **103**, 7725.
- Blowers, P. and Masel, R. I. (1999b). *AIChE J.*, **45**, 1794.
- Blowers, P. and Masel, R. I. (2000). *AIChE J.*, **46**, 2041.
- Blowers, P., Ford, L., and Masel, R. I. (1998). *J. Phys. Chem. A*, **102**, 9267.
- Caralp, F., Devolder, P., Fittschen, C., Gomez, N., Hippler, H., Mereau, R., Rayez, M. T., Striebel, F., and Viskolcz, B. (1999). *Phys. Chem. Chem. Phys.*, **1**, 2935.
- Chen, C. J. and Bozzelli, J. W. (2000a). *J. Phys. Chem. A*, **104**, 4997.
- Chen, C. J. and Bozzelli, J. W. (2000b). *J. Phys. Chem. A*, **104**, 9715.
- Curtiss, L. A., Raghavachari, K., Trucks, G. W., and Pople, J. A. (1991). *J. Chem. Phys.*, **94**, 7221.
- Curtiss, L. A., Raghavachari, K., and Pople, J. A. (1993a). *J. Chem. Phys.*, **98**, 1293.
- Curtiss, L. A., Raghavachari, K., and Pople, J. A. (1993b). *Chem. Phys. Lett.*, **214**, 183.
- Curtiss, L. A., Raghavachari, K., and Pople, J. A. (1995). *J. Chem. Phys.*, **103**, 4192.
- Curtiss, L. A., Redfern, P. C., Smith, B. J., and Radom, L. (1996). *J. Chem. Phys.*, **104**, 5148.
- Curtiss, L. A., Raghavachari, K., Redfern, P. C., and Pople, J. A. (1997a). *J. Chem. Phys.*, **106**, 1063.
- Curtiss, L. A., Redfern, P. C., Raghavachari, K., Rassolov, V., and Pople, J. A. (1997b). *J. Chem. Phys.*, **110**, 4703.
- Curtiss, L. A., Raghavachari, K., Redfern, P. C., Rassolov, V., and Pople, J. A. (1998). *J. Chem. Phys.*, **109**, 7764.

- Espinosa-Garcia, J., Corchado, J. C., and Truhlar, D. G. (1997). *J. Am. Chem. Soc.*, **119**, 9891.
- Feller, D., Dupuis, M., and Garrett, B. C. (2000). *J. Chem. Phys.*, **113**, 218.
- Gardiner, Jr., W. C. (1984). *Combustion Chemistry*, Springer-Verlag, New York.
- Gaussian 92/DFT. (1993). Revision G-2, Gaussian, Inc., Pittsburgh.
- Gaussian 94. (1995). Gaussian, Inc., Pittsburgh.
- Gaussian 98. (1998). Revision A.7, Gaussian, Inc., Pittsburgh.
- Glukhovtsev, M. N., Pross, A., and Radom, L. (1995a). *J. Am. Chem. Soc.*, **117**, 9012.
- Glukhovtsev, M. N., Pross, A., and Radom, L. (1995b). *J. Am. Chem. Soc.*, **117**, 2024.
- Glukhovtsev, M. N., Pross, A., and Radom, L. (1996a). *J. Am. Chem. Soc.*, **118**, 6273.
- Glukhovtsev, M. N., Pross, A., Schlegel, H. B., Bach, R. D., and Radom, L. (1996b). *J. Am. Chem. Soc.*, **118**, 11258.
- Hand, M. R., Rodriguez, C. F., Williams, I. H., and Balint-Kurti, G. G. (1998). *J. Phys. Chem. A*, **102**, 5958.
- Hucknall, D. J. (1985). *Chemistry of Hydrocarbon Combustion*, Chapman and Hall, New York.
- Jodkowski, J. T., Rayez, M. T., Rayez, J. C., Berces, T., and Dobe, S. (1998). *J. Phys. Chem. A*, **102**, 9219.
- Jursic, B. S. (2000a). *J. Molec. Struct.-Theo.*, **498**, 123.
- Jursic, B. S. (2000b). *J. Molec. Struct.-Theo.*, **499**, 223.
- Kedziora, G. S., Pople, J. A., Rassolov, V. A., Ratner, M. A., Redfern, P. C., and Curtiss, L. A. (1999). *J. Chem. Phys.*, **110**, 7123.
- Kondo, S., Tokuhashi, K., Takahashi, A., and Kaise, M. (2000). *J. Haz. Mater.*, **79**, 77.
- Korchowiec, J., Kawahara, J., Matsumura, K., Uchimaru, T., and Sugie, M. (1999). *J. Phys. Chem. A*, **103**, 3548.
- Lee, W. T. and Masel, R. I. (1996). *J. Phys. Chem.*, **100**, 10945.
- Mayer, P. M., Parkinson, C. J., Smith, D. M., and Radom, L. (1998). *J. Chem. Phys.*, **108**, 604.
- Mebel, A. M., Morokuma, K., and Lin, M. C. (1995). *J. Chem. Phys.*, **103**, 7414.
- Montgomery, J. A., Ochterski, J. W., and Petersson, G. A. (1994). *J. Chem. Phys.*, **101**, 5900.
- Montgomery, J. A., Frisch, M. J., Ochterski, J. W., and Petersson, G. A. (1999). *J. Chem. Phys.*, **110**, 2822.
- Montgomery, J. A., Frisch, M. J., Ochterski, J. W., and Petersson, G. A. (2000). *J. Chem. Phys.*, **112**, 6532.
- Morihovitis, T., Schuesser, C. H., and Skidmore, M. A. (1999). *J. Chem. Soc. Perkin Trans.*, **10(2)**, 2041.
- Nicolaides, A., Rauk, A., Glukhovtsev, M. N., and Radom, L. (1996). *J. Phys. Chem.*, **100**, 17460.

- Ochterski, J. W., Petersson, G. A., and Montgomery, Jr., J. A. (1996). *J. Chem. Phys.*, **104**, 2598.
- Petersson, G. A. and Allaham, M. A. (1991). *J. Chem. Phys.*, **94**, 6081.
- Petersson, G. A., Bennett, A., Tensfeldt, T. G., Allaham, M. A., Shirley, W. A., and Mantzaris, J. (1988). *J. Chem. Phys.*, **89**, 2193.
- Petersson, G. A., Tensfeldt, T. G., and Montgomery, J. A. (1991). *J. Chem. Phys.*, **94**, 6091.
- Pople, J. A., Head-Gordon, M., Fox, D. J. Raghavachari, K., and Curtiss, L.A. (1989). *J. Chem. Phys.*, **90**, 5622.
- Smith, B. J. and Radom, L. (1994). *Chem. Phys. Lett.*, **231**, 345.
- Smith, B. J. and Radom, L. (1996). *Chem. Phys. Lett.*, **245**, 123.
- So, S. P. (1999). *Chem. Phys. Lett.*, **313**, 307.
- Stephens, P. J., Devlin, F. J., Chabalowski, C. F., and Frisch, M. J. (1994). *J. Phys. Chem.*, **98**, 11623.
- Truong, T. N. (1994). *J. Chem. Phys.*, **100**, 8014.
- Westley, F. (1980). *Table of Recommended Rate Constants for Chemical Reactions Occurring in Combustion*, U. S. Department of Commerce, Washington, D. C.
- Wong, M. W. and Radom, L. (1998). *J. Phys. Chem. A*, **102**, 2237.
- Zhang, Y., Zeng, X. R., and You, X. Z. (2000). *J. Chem. Phys.*, **113**, 7731.

HYDRODYNAMIC AND TEMPERATURE EFFECTS ON THE FLOW-INDUCED LOCAL CORROSION RATE IN PIPELINES

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When a flow enters a pipeline or goes over an obstacle, a new boundary layer is developed and produces a local corrosion rate that is greater than the average corrosion rate. Equations are developed to calculate this local flow-induced corrosion rate. The calculated local corrosion rate varies from a fraction of mm/year to 1.27 mm/year (50 mils/year), depending on the temperature, velocity, and location of the flow. The calculations also show that the maximum local corrosion rate occurs at a short distance from the edge of the pipe entrance. The wavy appearance of erosion-corrosion failure on metal surfaces can be explained by the boundary layer theory and the convective mass transfer of ferrous ions.

Keywords: Flow-induced corrosion; Local corrosion rate; Erosion; Temperature effect

INTRODUCTION

There are hundreds of thousands of miles of pipelines in various sectors of industry, which include many uncoated pipelines in chemical manufacturing plants, interstate natural gas transmission lines, and offshore oil-and-gas production pipelines. The maintenance and replacement of these pipelines are crucial and costly. Therefore, the protection of