JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 6, 551–554 (1993)

HEATS OF FORMATION OF ORGANIC MOLECULES BY *AB INITIO* CALCULATIONS: ALKYL RADICALS

RUIFENG LIU AND NORMAN L. ALLINGER*

Computational Center for Molecular Structure and Design, Department of Chemistry, University of Georgia, Athens, Georgia 30602, U.S.A.

A bond and group equivalent scheme that allows the calculation of heats of formation for alkyl radicals from the *ab initio* restricted open-shell Hartree–Fock 6–31G* energies was developed. For a group of 12 radicals, the rms error for the calculated heats of formation was 0·65 kcal mol^{-1} (1 kcal = 4·184 kJ). Heats of formation were predicted for the pentyl radical and six of its isomers for which the experimental values are unknown.

INTRODUCTION

Alkyl radicals are perhaps the simplest but yet some of the most reactive organic radicals. They play a central role in the petroleum industry[1] and are reactive intermediates in the production of many commercial polymers.[2] As reactive intermediates they also play essential roles in polymer degradation,[3] thus determining the stability of many materials such as coatings and lubricants toward heat, light and high-energy radiation. Consequently, they have been the focus of active research in many industrial and academic laboratories.

Owing to their unusual reactivity, alkyl radicals do not easily lend themselves to the usual kinds of experimental measurements. As a result, experimental information is scarce. For example, although they are important intermediates in the combustion of organic compounds, heat of formation data are available for only a few radicals. Further, these data were determined by indirect methods and are less reliable than those for stable organic compounds. Hence there are often conflicts between heats of formation reported by different groups as they may differ by more than the combined error limits.

The difficulty in experimental studies of alkyl radicals stems from the fact that they lie in relatively shallow potential wells and they tend to have very short lifetimes because they can react with one another, or with other molecules, to form more stable materials. However, theoretically they are stable in the sense that at the equilibrium structures, the potential surfaces have no negative curvatures. Hence theoretical approaches are more advantageous than experimental approaches for their study. Indeed, *ab initio* calculations played very important roles in our understanding of the structures and properties of the alkyl radicals.[4]

For small molecules, state of the art *ab initio* calculations of molecular structures and energies at the G1[5] or G2[6] levels are fairly successful. However, such calculations become very expensive for molecules containing more than a few heavy atoms.

The bond energy scheme which combines *ab initio* and experimental information in the calculation of heats of formation is very promising.[7–13] In this approach, the *ab initio* calculations are carried out at the affordable restricted Hartree–Fock (RHF) level using the 6–31G* basis set.[14,15] The errors in the Hartree–Fock energies and correlation effects are absorbed in the bond and group parameters so that the accuracies of the calculated heats of formation are comparable to those of good experimental measurements.

In this paper, the bond energy scheme is extended to cover alkyl radicals, so that the heats of formation can be accurately predicted from the results of inexpensive *ab initio* calculations.

METHODS AND CALCULATIONS

The basis of the bond energy scheme for the calculation of heats of formation was outlined previously.[10] The method we use is similar to those of Wiberg[7] and Ibrahim and Schleyer,[8] but differs from those in the explicit inclusion of terms to account for the statistical mechanical effects of populating higher energy conformations of the molecule (*POP*), low-lying vibrational states (*TOR*), translational and rotational states and the

---

* Author for correspondence.

0894–3230/93/100551–04$07.00

Received 8 March 1993
Revised 11 June 1993

term (PV) required convert ΔE to ΔH. The full expression is

$$\Delta H_f^\circ = \Sigma BE + \Sigma GE + HFE + POP + TOR + 4RT$$

where the first two terms are contributions of the bond energy increments and the group energy increments, respectively (for calculating group increments, the unpaired electron is viewed as a substituent X attached to the radical center). *HFE* is the *ab initio* energy obtained using the Hartree–Fock approximation and the 6–31G* basis set and $4RT$ is the classical value for the translational and rotational energy and the conversion of ΔE to ΔH_f°.

For calculating the heats of formation of alkyl radicals, the following bond and group equivalents are needed: bond equivalents for the C—C$^\cdot$ and H—C$^\cdot$ bonds, and group equivalents for the methyl, primary, secondary and tertiary radicals. The bond and group equivalents of the saturated parts of the alkyl radicals are the same as those of alkanes, which have been derived before.[9] The set of bond and group equivalents pertinent to the radical center are not all independent. For the least-squares treatment, two redundancies have to be removed. To this end, we arbitrarily set the H—C$^\cdot$ bond equivalent equal to the value of the C—H bond of alkanes[9] and the group equivalent of the secondary radical to zero. Hence we were left with four equivalents to be determined. They were determined by least-squares fitting of the heats of formation of 12 relatively unstrained alkyl radicals. The results were used in the prediction of the heats of formation of the *n*-pentyl radical and six of its isomers for which experimental data are not yet available.

The *HFE* energies of the alkyl radicals were calculated by the restricted open-shell Hartree–Fock (ROHF) method using the program TX90.[16] All of the molecular structures were fully optimized. The geometry optimizations were terminated when the projected energy change was smaller than 10^{-7} a.u., which ensures that the maximum projected bond length change is smaller than 0·001 Å and the maximum angle change is smaller than 0·1°. The *ab initio* calculations were started with the most stable conformation of each radical, which was obtained by an MM3 conformational search. For the cycloheptyl radical, *ab initio* calculations were also carried out on several low-energy conformations. The results indicate that the most stable conformation from the MM3 conformational search is also the most stable conformation by *ab initio* calculations.

The *POP* and *TOR* terms were not determined by *ab initio* calculation, but were carried over from the MM3 calculations[17] instead.

It should be pointed out that since the bond and group equivalents were determined by least-squares fitting of the experimental heats of formation, the results depend on, among other things, the goodness of the experimental data. The heats of formation of about 13 alkyl radicals have been reported. For the smaller radicals, different results were found in the literature. We selected a set of the most recent and internally consistent data: the heats of formation of ethyl, *n*-propyl, isopropyl, *n*-butyl, *sec*-butyl and *tert*-butyl radicals were taken from the recent measurements of Holmes *et al.*,[18] that of methyl radical was taken from the kinetic study of Russell *et al.*[19] and the heat of formation of neopentyl radical was taken from Tsang's assessment.[20] The data on cyclopentyl, cyclohexyl, cycloheptyl and 1-norbornyl radicals were taken from the recommendations of Benson (cited in Ref. 21).

RESULTS AND DISCUSSION

The input data for the least-squares determination of the bond and structural equivalents are presented in Table 1. The parameters derived and the results for

Table 1. Heat of formation input data (kcal mol^{-1})

Radical	H_f°(exp.)[a]	SUMH[b]	E (6–31G*)	*POP*	*TOR*	$4RT$
Methyl	35·37(0·72)	18 901·94	−24 820·98	0·00	0·00	2·40
Ethyl	27·80(0·6)	31 504·75	−49 317·82	0·00	0·00	2·40
n-Propyl	22·70(0·4)	55 993·92	−73 812·41	0·05	0·42	2·40
Isopropyl	19·10(0·6)	44 107·56	−73 815·24	0·00	0·00	2·40
n-Butyl	18·10(0·6)	80 483·08	−98 307·17	0·20	0·84	2·40
sec-Butyl	15·30(0·3)	68 596·73	−98 309·71	0·20	0·42	2·40
Isobutyl	15·80(0·3)	80 482·17	−98 307·29	0·08	0·42	2·40
tert-Butyl	9·50(0·2)	56 710·37	−98 312·39	0·00	0·00	2·40
Neopentyl	7·79(0·96)	104 968·92	−122 801·73	0·00	0·42	2·40
Cyclopentyl	24·30(1·0)	92 369·43	−122 072·49	0·00	0·42	2·40
Cyclohexyl	14·30(1·0)	116 858·60	−146 571·06	0·01	0·42	2·40
Cycloheptyl	12·20(1·0)	141 347·76	−171 061·05	0·21	0·42	2·40
1-Norbornyl	32·60(2·5)	128 744·04	−170 317·53	0·00	0·00	2·40

[a] Numbers in parentheses are the reported experimental error limits.

[b] SUMH is the energy from the alkane part of the molecule (see Refs. 9, 10).

the individual compounds are presented in Table 2. The root-mean-square error over the set of twelve relatively unstrained radicals was 0·65 kcal mol^{-1} (1 kcal = 4·184 kJ). This value is similar to the errors in the experimental data and shows that the calculational method employed here is competitive in accuracy with the experimental methods for the highly reactive alkyl radicals. We omitted from the least-squares fitting the 1-norbornyl radical, for which the discrepancy between the calculated and experimental heat of formation is unusually large. One of the sources of this discrepancy may be the high degree of strain in this radical. However, it is more probable that the experimental heat of formation is in error. The MM3 calculation[17] on this radical gives a heat of formation of 38·5 kcal mol^{-1}, which is in agreement with the present result. For cycloheptyl radical, the calculated result is 1·8 kcal mol^{-1} higher than the experimental heat of formation. MM3 calculation also overestimates the heat of formation of this radical by 1·4 kcal mol^{-1}. The experimental error is 1·0 kcal mol^{-1}, which is higher than those of the smaller alkyl radicals. For the other radicals in Table 1, the calculated heats of formation are in good agreement with the results of the MM3 calculations.

The radicals in Table 1 are perhaps all the alkyl radicals for which the experimental heats of formation have been reported. The heats of formation of other alkyl radicals are also very important in the petroleum industry and in the study of combustion process but, owing to the reactivity of the radicals, the experimental measurements are difficult and the data are not available. With the derived parameters in Table 2, we calculated the heats of formation of the *n*-pentyl radical and six of its isomers, 2-pentyl, 3-pentyl, 3-methyl-1-butyl, 3-methyl-2-butyl, 2-methyl-2-butyl and 2-methyl-1-butyl radicals. The input data (Hartree–Fock energy, *POP* and *TOR* terms) and the calculated heats of formation are given in Table 3.

Based on the good agreement between the calculated and experimental heats of formation in Table 2, and

Table 2. Heat of formation output data (kcal mol^{-1})[a]

Eq.	Wt.[b]	H_f° (calc.)	H_f° (exp.)	Difference (calc. − exp.)	Radical
1	5	35·37	35·37	0·00	Methyl
2	9	27·64	27·80	−0·16	Ethyl
3	7	22·66	22·70	−0·04	N-propyl
4	7	19·11	19·10	0·01	Isopropyl
5	5	17·65	18·10	−0·45	*n*-Butyl
6	7	14·32	15·30	−0·98	*sec*-Butyl
7	7	16·07	15·80	0·27	Isobutyl
8	7	9·50	9·50	0·00	*tert*-Butyl
9	5	8·31	7·79	0·52	Neopentyl
10	5	24·04	24·30	−0·26	Cyclopentyl
11	5	14·64	14·30	0·34	Cyclohexyl
12	5	14·02	12·20	1·82	Cycloheptyl
13	0	38·03	32·60	5·43	1-Norbornyl

[a] Best values: C—C$^\cdot$ = 14 862·14 (23·684308 hartree); ME = 5952·02 (9·485134 hartree), PRI = 2976·16 (4·7428089 hartree); TER = −2977·29 (−4·744617 hartree). Standard deviation = 0·648, based on 12 equations. Optimization and analysis ignore all equations whose weight is zero.

[b] The weight given in the least squares fit.

Table 3. Heat of formation input and output data for *n*-pentyl radical and its isomers (kcal mol^{-1})

Radical	SUMH	*E* (6–31G*)	*POP*	*TOR*	*T*/*R*	H_f°
1-Pentyl	104 972·24	−122 801·83	0·16	1·26	2·40	12·54
2-Pentyl	93 085·89	−122 803·97	0·00	0·84	2·40	9·44
3-Pentyl	93 085·89	−122 804·26	0·00	0·84	2·40	9·15
3-Methyl-1-butyl	104 971·33	−122 801·69	0·12	0·84	2·40	11·30
3-Methyl-2-butyl	93 084·98	−122 804·07	0·00	0·42	2·40	8·01
2-Methyl-2-butyl	81 199·54	−122 806·10	0·16	0·42	2·40	6·54
2-Methyl-1-butyl	14971·33	−122 800·50	0·10	0·84	2·40	12·47

also based on experience from the *ab initio* calculations on heats of formation of many organic molecules, we believe that the calculational method and parameter set developed in this study can be used to predict the heats of formation of alkyl radicals which are not too highly strained, e.g. the isomers of pentyl radicals, with an accuracy of 1 kcal mol^{-1}.

CONCLUSION

The combined *ab initio*–empirical scheme for calculating heats of formation developed previously was applied to alkyl radicals, and was shown to give results that are competitive with experimental determinations. With the parameters derived in this work, heats of formation of alkyl radicals can be accurately predicted *a priori*. The heats of formation of the *n*-pentyl radical and six of its isomers, for which the heats of formation have not been reported previously, were predicted by this method. The remaining isomer, neopentyl, is included in Table 2. These calculations can be used when experimental results are unavailable, and they can be used as an independent check when an experimental result is in question.

ACKNOWLEDGMENTS

The authors are indebted to Professor Peter Pulay for the use of the program TX90. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

REFERENCES

1. D. A. Leathard and J. H. Purnell, *Annu. Rev. Phys. Chem.*, **21**, 197 (1970).
2. C. E. Hoyle and J. F. Kinstle (Eds), *Radiation Curing of Polymeric Materials, ACS Symposium Series, Vol. 417*, American Chemical Society, Washington, DC (1989).
3. W. Schnabel, *Polymer Degradation: Principles and Practical Applications*. Macmillan, New York (1981).
4. J. Pacansky, W. Koch and M. D. Miller, *J. Am. Chem. Soc.* **113**, 317 (1991), and references cited therein.
5. J. A. Pople, M. Head-Gordon, D. J. Fox, K. Raghavachari and L. A. Curtiss, *J. Chem. Phys.* **90**, 5622 (1989).
6. L. A. Curtiss, K. Ragavachari, G. W. Trucks and J. A. Pople, *J. Chem. Phys.* **94**, 7221 (1991).
7. K. Wiberg, *J. Comput. Chem.* **5**, 197 (1984); *J. Org. Chem.* **50**, 5285 (1985).
8. M. R. Ibrahim and P. v. R. Schleyer, *J. Comput. Chem.* **6**, 157 (1985).
9. N. L. Allinger, L. R. Schmitz, I. Motoc, C. Bender and J. K. Labanowski, *J. Phys. Org. Chem.* **3**, 732 (1990).
10. N. L. Allinger, L. R. Schmitz, I. Motoc, C. Bender and J. K. Labanowski, *J. Am. Chem. Soc.* **114**, 2880 (1992).
11. N. L. Allinger, L. R. Schmitz, I. Motoc, C. Bender and J. K. Labanowski, *J. Comput. Chem*, **13**, 838 (1992).
12. N. L. Allinger, L. Yang, I. Motoc, C. Bender and J. K. Labanowski, *Heteroatom Chem.* **3**, 69 (1992).
13. L. R. Schmitz, I. Motoc, C. Bender, J. K. Labanowski and N. L. Allinger, *J. Phys. Org. Chem.* **5**, 225 (1992).
14. W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.* **56**, 2257 (1972).
15. P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta* **28**, 213 (1972).
16. P. Pulay, *TX90*, University of Arkansas, Fayetteville, AR (1990); *Theor. Chim. Acta* **50**, 299 (1979).
17. R. Liu and N. L. Allinger, *J. Comput. Chem.* in press.
18. J. L. Holmes, F. P. Lossing and A. Maccoll, *J. Am. Chem. Soc.* **110**, 7339 (1988).
19. J. J. Russell, J. A. Seetula and D. Gutman, *J. Am. Chem. Soc.* **110**, 3092 (1988).
20. W. Tsang, *J. Am. Chem. Soc.* **107**, 2872 (1985).
21. M. R. Imam and N. L. Allinger, *J. Mol. Struct.* **126**, 345 (1985).