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Ab Initio Calculations Indicate That a Polar Effect Causes Abstraction of Cubyl Hydrogens from Methylcubane To Be Favored Kinetically

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In connection with a previous computational study[1] of the unusual stability of cubyl cation[2] we calculated the relative bond dissociation energies (BDEs) of the teriary C–H bonds in cubane, norbornane, and isobutane. Calculations of the energies of the hydrocarbons were performed at the Hartree–Fock level of theory with the 6-31G* basis set,[3] and unrestricted Hartree–Fock (UHF) calculations were carried out to compute the energies of the cubyl, 1-norbornyl, and *tert*-butyl radicals. The C–H BDEs in cubane and norbornane were computed to be, respectively, 11.0 and 10.3 kcal/mol larger than that of the tertiary C–H bond in isobutane.[1]

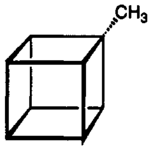
Inclusion of electron correlation at the MP2 level of theory[4] was found to play a major role in calculating correctly the difference between the energies required to form the nonclassical cubyl and classical 1-norbornyl cations.[1] Therefore, we also performed MP2 calculations on the energies required to form the radicals. At the MP2/6-31G*//(U)HF/3-21G level of theory the C–H BDE of cubane, relative to that of the tertiary C–H bond in isobutane, decreased to 8.0 kcal/mol, whereas that of norbornane remained unchanged at 10.3 kcal/mol. The calculated differences in C–H BDEs are qualitatively consistent with the experimental rates of formation of these three radicals by perester thermolyses.[5]

Della and co-workers have pointed out that a cubane C–H BDE which was 11.0 kcal/mol greater than that of isobutane would give an absolute value of about 107 kcal/mol for the cubane C–H BDE and that this value is considerably greater than the BDE of 100.5 kcal/mol for a primary C–H bond.[6] Indeed, we calculate that, when zero-point energy differences are included, the C–H BDE of cubane is higher than that of ethane by 7.5 kcal/mol at the (U)HF/6-31G* level and by 5.0 kcal/mol at (U)MP2/6-31G*.[7] Nevertheless, Della and co-workers have presented EPR evidence that, when *tert*-butoxyl radicals react with methylcubane (**1**), cubyl hydrogens are preferentially abstracted to form the three possible methylcubyl radicals (**2a–c**). Neither the cubylmethyl radical (**3**), whose formation might have been expected on the basis of the lower BDEs of primary, relative to cubyl, hydrogens, nor rearrangement products of **3**[8] were detected.[6]

Table 1. Relative 6-31G* and Zero-Point Energies (kcal/mol) of Radicals **2a–c** and **3** and of the Transition States Leading to Them in the Reaction of **1** with Methoxyl Radical

radicals	*E* (UHF)	*E* (UMP2)	*E* (PUMP2)	*E* (PUMP2+ZPE)
2a	6.8	4.3	5.0	6.7
2b	6.8	4.2	4.9	6.6
2c	6.8	4.2	4.9	6.6
3	0[a]	0[b]	0[c]	0[d]
transition states				
→ **2a**	1.2	−2.8	−2.3	−2.4
→ **2b**	1.4	−2.5	−2.0	−2.1
→ **2c**	1.4	−2.4	−1.9	−2.0
→ **3**	0[e]	0[f]	0[g]	0[h]

[a] $E = -345.8050$ hartrees. [b] $E = -346.9319$ hartrees. [c] $E = -346.9345$ hartrees. [d] ZPE = 99.3 kcal/mol. [e] $E = -460.8006$ hartrees. [f] $E = -462.2548$ hartrees. [g] $E = -462.2618$ hartrees. [h] ZPE = 132.5 kcal/mol.



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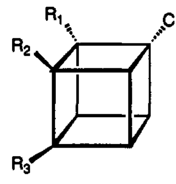
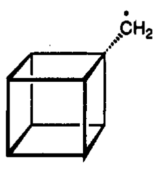


2a, $R_1 = \bullet$, $R_2 = R_3 = H$
b, $R_1 = R_3 = H$, $R_2 = \bullet$
c, $R_1 = R_2 = H$, $R_3 = \bullet$



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In order to understand this experimental result, we have performed *ab initio* calculations on hydrogen abstraction from **1**. Geometries were optimized with UHF/6-31G* calculations and vibrational analyses were performed at this level of theory.[9] The energies of stationary points were recalculated at the UMP2/6-31G* level, before and after projection (PUMP2) of the quartet contaminants from the wave functions. All calculations were performed with the Gaussian 92 package of *ab initio* programs,[10] and the results are given in Table 1.

As shown in Table 1, the three methylcubyl radicals (**2a–c**) were all found to have the same energy to within ±0.1 kcal/mol. At all levels of theory the energy difference between **2** and **3** is about 1 kcal/mol larger than the difference between the BDEs of cubane and ethane.[11] Thus, our calculations leave little doubt that, were hydrogen abstraction from **1** to lead to the most stable radical, **3** would be formed, rather than **2**. Consequently, the experimental results of Della and co-workers[6] may be interpreted as showing that, in the abstraction of hydrogen from **1** by *tert*-butoxyl radicals, the relative energies of the transition states are the reverse of the relative energies of the radicals to which the transition states lead.

It is well-known that the relative rates of radical abstraction of hydrogen atoms from substituted toluenes do not always follow the relative stabilities of the benzylic radicals formed.[12] The rates are also found to depend on the ability of the substituents to stabilize a partial positive charge on the benzylic methylene group in the transition state, when the abstracting radical is electronegative (e.g., *tert*-butoxyl), and a negative charge, when

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(1) Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1990,** *112,* 3227.

(2) Eaton, P. E.; Yang, C.-X.; Xiong, Y. *J. Am. Chem. Soc.* **1990,** *112,* 3225. Moriarity, R. M.; Sudersan, M. T.; Penmasta, R.; Awasthi, A. K. *J. Am. Chem. Soc.* **1990,** *112,* 3228. Kevill, D. N.; D'Souza, M. J.; Moriarity, R. M.; Sudersan, M. T.; Penmasta, R.; Awasthi, A. K. *J. Chem. Soc., Chem. Commun.* **1990,** 623. Eaton, P. E.; Zhou, J. P. *J. Am. Chem. Soc.* **1992,** *114,* 3118.

(3) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973,** *28,* 213.

(4) Moller, C.; Plesset, M. S. *Phys. Rev.* **1934,** *46,* 618. Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem.* **1976,** *S10,* 1.

(5) Stock, L. M.; Luh, T.-Y. *J. Org. Chem.* **1978,** *43,* 3271.

(6) Della, E. W.; Head, N. J.; Mallon, P.; Walton, J. C. *J. Am. Chem. Soc.* **1992,** *114,* 10730.

(7) Calculations were performed at (U)HF/6-31G* optimized geometries and include a zero-point energy correction that increases the BDE of cubane, relative to ethane, by 1.9 kcal/mol. The resulting (U)MP2/6-31G* C–H BDE of about 105.5 kcal/mol for cubane is roughly 1 kcal/mol higher than that obtained from the same type of calculations, but referenced to the C–H BDE of isobutane: Staneke, P. O.; Ingemann, S.; Eaton, P. E.; Nibbering, N. M. M.; Kass, S. R. *J. Am. Chem. Soc.* in press. Previous (U)HF/4-31G* calculations found the C–H BDE in cubane to be 9 kcal/mol greater than the BDE of a primary C–H bond in propane: Schubert, W.; Yoshimine, M.; Pacansky, J. *J. Phys. Chem.* **1981,** *85,* 1340.

(8) Eaton, P. E.; Yip, Y. C. *J. Am. Chem. Soc.* **1991,** *113,* 7692. Choi, S.-Y.; Eaton, P. E.; Newcomb, M.; Yip, Y. C. *J. Am. Chem. Soc.* **1992,** *114,* 6326.

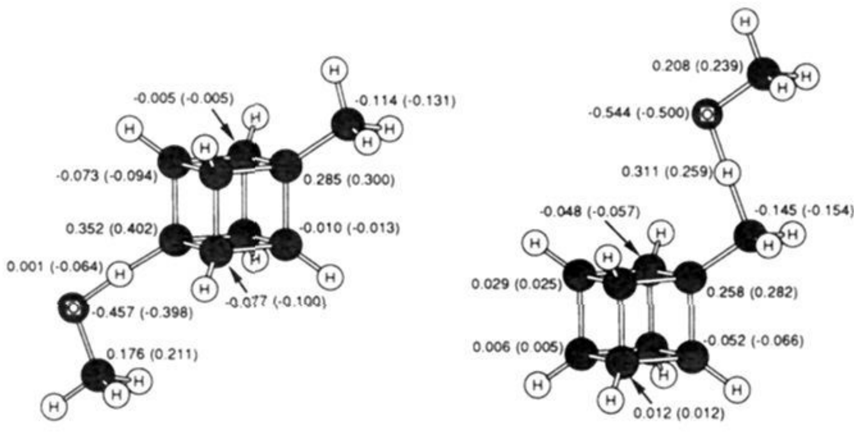
(9) UHF/6-31G* optimized geometries are available as supplementary material.

(10) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, W. P. M.; 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, Inc., Pittsburgh, PA, 1992.

(11) Since we calculate that the methyl group in **1** has essentially no effect on the BDE of a cubyl hydrogen, our computational results indicate that the strained C–C bonds of the cubane skeleton in **3** provide about 1 kcal/mol more stabilization for a primary radical center than is furnished by the methyl group in ethyl radical.

(12) Pryor, W. A.; Davis, W. H., Jr.; Stanley, J. P. *J. Am. Chem. Soc.* **1973,** *95,* 4754 and the many book chapters and reviews referenced in this paper.

0002-7863/94/1516-6459$04.50/0



a b

Figure 1. CHELPG charges, condensed to the heavy atoms, and on the hydrogen being transferred from **1** to methoxyl radical for (a) the transition state for formation of **2c** and (b) the transition state for formation of **3**. The charges obtained from both UHF and UMP2 wave functions are shown, the former in parentheses.

the abstracting radical is electropositive (e.g., *tert*-butyl). Given the well-documented importance of such "polar effects" in the transition states for hydrogen abstractions from substituted toluenes,[12] it seemed quite plausible that the unusual stability of cubyl cation[1,2] could cause abstraction of a cubyl hydrogen from **1** by *tert*-butoxyl radicals to be faster than abstraction of a methyl hydrogen.

In order to test this hypothesis we performed calculations on the transition states for these reactions. Instead of *tert*-butoxyl radical, we used the computationally more tractable methoxyl radical. Although this represents an approximation to the actual reaction that has been studied experimentally,[6] we calculate that hydrogen abstraction by *tert*-butoxyl is only 1–2 kcal/mol more exothermic than hydrogen abstraction by methoxyl.

A potentially more serious problem is caused by the fact that calculations with the 6-31G* basis set underestimate the strengths of C–H, relative to O–H, bonds.[13] Nevertheless, since we were not concerned with calculating the thermodynamics of hydrogen abstraction from methylcubane, but only with computing the relative energies of the isomeric transition states, it seemed reasonable to expect that calculations with 6-31G* might yield results that were at least qualitatively correct.

The transition states were located with UHF/6-31G* calculations, and their energies were recalculated at the UMP2 and PUMP2/6-31G* levels of theory. The transition-state geometries for the formation of **2c** and **3** from reaction of methoxyl with **1** are depicted, respectively, in parts a and b of Figure 1. As shown in Table 1, like the energies of **2a–c**, the relative energies of the transition states leading to them are all nearly the same.

At the UHF/6-31G* level of theory the transition states for methoxyl abstraction of cubyl hydrogens from **1** are 1.2–1.4 kcal/mol higher in energy than the transition state for abstraction of a methyl hydrogen. However, at both the UMP2 and PUMP2/6-31G* levels of theory, the energies of the transition states for abstraction of the two different types of hydrogens from **1** are reversed. The transition states for abstraction of cubyl hydrogens are all predicted to be about 2 kcal/mol lower in energy than the transition state for abstraction of a methyl hydrogen.[14]

On going from UHF to the UMP2 and PUMP2 calculations, the changes in the relative energies of the two different types of transition states are 50–90% larger than the changes in the relative energies of the two different types of radicals formed. It is tempting to attribute the larger effect of inclusion of electron correlation on the relative energies of the two types of transition states to the greater importance of electron correlation in calculating correctly the energy of a cubyl species that has some cationic character.[1]

The charges found by a CHELPG analysis[15] of the calculated electron densities support this hypothesis. The CHELPG charges, condensed to the heavy atoms, and also those on the hydrogen being transferred from **1** to methoxyl are given in Figure 1a for the transition state for formation of **2c** and in Figure 1b for the transition state for formation of **3**. The charges obtained from both UHF and UMP2 wave functions are shown, the former in parentheses.

In the transition states for formation of **2a** and **2b**, as well as **2c**, considerable amounts of positive charge develop at the cubyl carbon from which the hydrogen is being abstracted. Overall, the methylcubyl fragment is calculated to bear a total of about 0.25 unit of positive charge in each transition state at the UHF level, which increases to 0.28 unit at the MP2 level. At the MP2 level the hydrogen being transferred is essentially uncharged, and at both UHF and MP2 most of the negative charge resides on the oxygen of the methoxyl group.

In contrast, in the transition state for formation of **3**, the hydrogen bears considerable positive charge, and the cubylmethyl fragment remains nearly neutral. The UMP2/6-31G* CHELPG positive charge on the hydrogen is about 75% of that calculated in methanol. Unlike the case in the transition states for formation of **2a–c**, in the transition state for formation of **3**, there is obviously very little positive charge transferred from the hydrogen to the carbon from which it is being abstracted.

In summary, our calculations at the UMP and PUMP2/6-31G* levels find, in agreement with experiment,[6] that, in the abstraction of hydrogens from **1** by an alkoxyl radical, the transition states for formation of **2a–c** are lower in energy than the transition state for formation of **3**. Although the small energy differences between the two types of transition states may not be calculated with quantitative accuracy at these levels of theory,[14] of qualitative significance is the computational result that the transition-state energies are the reverse of those of the radicals to which they lead. The cause of this reversal seems to be a polar effect that operates in the transition states for formation of the cubyl radicals and that has its origin in the ability of cubyl carbons to accommodate a positive charge. The effects of electron-donating and electron-withdrawing cubyl substituents on the rates of hydrogen abstraction by *tert*-butoxyl radicals[6] are consistent with this proposal.[16]

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Supplementary Material Available: UHF/6-31G* optimized geometries for **2a–c**, **3**, and the transition states leading to them from reaction of **1** with a methoxyl radical (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(13) We find that the exothermicity of the reaction $CH_3O^\bullet + C_2H_6 \rightarrow CH_3OH + C_2H_5^\bullet$, is underestimated by about 15 kcal/mol at the RHF-UHF/6-31G* level of theory, by about 4 kcal/mol at the MP2/6-31G* level, and by about 8 kcal/mol at the MP4 level. Because O–H bonds are much more polar than C–H bonds, we find that very large basis sets are required to describe correctly the difference in electron correlation between these two types of bonds. We are indebted to Professor James E. Jackson of Michigan State University for bringing this problem with the 6-31G* basis set to our attention.

(14) At the UMP4SDQ/6-31G* level of theory we also find that the transition state leading to **2c** is lower in energy than that leading to **3**, but the energy difference between the two transition states decreases to 1.2 kcal/mol.

(15) Breneman, C. M.; Wiberg, K. B. *J. Comput. Chem.* **1990**, *11*, 361.

(16) Also consistent with this proposal are the results of calculations on the reaction of **1** with methyl radical. Since methyl is a much less electrophilic radical than *tert*-butoxyl,[12] a polar effect in the transition state should favor abstraction of cubyl over methyl hydrogens from **1** by less when the abstracting radical is methyl, instead of *tert*-butoxyl. Indeed, for hydrogen abstraction from **1** by methyl radical, we find at the PUMP2/6-31G* level that the transition state leading to **2c** is only 0.4 kcal/mol lower than that leading to **3**. Moreover, both the difference between the UHF and PUMP2 energies of the two transition states and also the positive charge on the methylcubyl fragment are computed to be about a factor of 3 less when methyl, rather than methoxyl, is the abstracting radical. An experimentally testable prediction of our calculations is that, if methyl radicals were allowed to react with **1**, formation of **3** would be found to be competitive with abstraction of cubyl hydrogens to form **2a–c**.