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Theoretical Studies of Elimination Reactions. 2. The Importance of Periplanar Transition States in $E1_{cb}$-like Eliminations. The Gauche Transition State of HO^- + $CH_3CH_2OCH_3$

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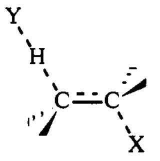
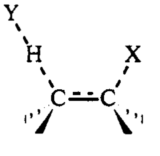
Abstract: The HO^- induced β-eliminations of $CH_3CH_2OCH_3$ were characterized using ab initio theoretical methods. At the 6-31(+)G* level, an antiperiplanar transition state (**3**) with an E_{1cb}-like structure was located; however, attempts to optimize a synperiplanar transition state led to second-order saddle points. In this system, the disadvantages of an eclipsed conformation outweigh the advantages of periplanarity, and a staggered, gauche transition state (**5**) is preferred (dihedral angle between transferring hydrogen and methoxy oxygen = 56.9°). Remarkably, the antiperiplanar transition state is only 5.2 kcal/mol more stable than the gauche transition state, and therefore conjugation between the developing carbon lone pair and the σ^* orbital of the C–OCH_3 bond plays only a minor role in driving the reaction. In $E1_{cb}$-like transition states, the need for periplanarity is greatly reduced because there is little double bond formation at the transition state. The energy difference between the gauche transition state (**5**) and one constrained to be synperiplanar (**4**) is very small (0.5 kcal/mol at the MP2/6-31(+)-G**/HF/6-31(+)G* level) indicating that, for syn eliminations, the transition state barrier is surprisingly insensitive to the torsional angle (H_β–C_β–C_α–OCH_3). The $E1_{cb}$-like nature of the transition states was confirmed by electron density analysis using Bader's PROAIM program, and the theoretical results were compared to relevant gas-phase experiments.

Introduction

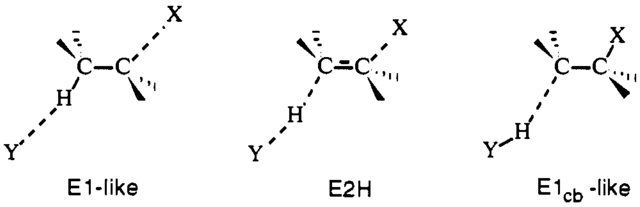
Bimolecular elimination reactions (E2) are fundamental processes in organic chemistry and have been studied extensively in solution. From these studies, a number of generalizations have evolved concerning the nature of the transition state.[1] First, it has been widely assumed that the transition state adopts a periplanar conformation so that the developing carbon lone pair can effectively interact with the C–X bond and initiate double bond formation. An anti transition state is usually favored because it involves a staggered conformation and allows for the most effective overlap between the developing π orbitals of the α and β carbons.[2]


Anti-Periplanar


Syn-Periplanar

Finally, the work of Cram[1n] and Bunnett[1j] indicates that the bonding changes in an E2 elimination may be concerted but nonsynchronous, and, therefore, a spectrum of transition states from E1-like to $E1_{cb}$-like is possible (Scheme I). These generalizations are in accord with recent, high-level ab initio calculations on the E2 reactions of CH_3CH_2Cl with F^- and PH_2^-.[3] In these systems, periplanar transition states were observed with anti being favored over syn by 12.7 and 8.4 kcal/mol, respectively. Experimentally, it has been noted that as the transition state becomes more $E1_{cb}$-like, the preference for an anti transition state diminishes presumably because orbital overlap and double bond formation play a smaller role in determining the stability of the transition state.[1d,o] In fact, syn elimination can dominate under highly basic conditions where $E1_{cb}$-like pathways are favored. For example, Brown and Saunders[4] found that the E2 eliminations of 3,3-dimethylcyclopentyltrimethylammonium salts prefer anti pathways with weaker bases (90% anti in NaOH/H_2O) and syn pathways with stronger bases (71.5% syn in *t*-BuOK/*t*-BuOH–DMSO); however, ion pairing complicates these solution-phase studies.[5]

Scheme I


E1-like E2H $E1_{cb}$-like

If the importance of π overlap diminishes as the transition state becomes more $E1_{cb}$-like, so should the preference for periplanarity. This is particularly true for a syn transition state, because here periplanarity requires an energetically unfavorable, eclipsed conformation. Although nonperiplanar transition states have been proposed in systems where periplanarity is prevented by geometric constraints (ring systems),[1d] the assumption has been that a twisted transition state is inherently less stable than a periplanar one. In fact, this author is unaware of any reports of acyclic E2 reactions *preferring* nonperiplanar transition states. In this study, we present ab initio calculations that indicate that along with syn- and antiperiplanar pathways, *a third pathway involving a gauche conformation is viable in eliminations with significant $E1_{cb}$-like character*. The gauche transition state has the advantage of a staggered conformation, but must sacrifice π overlap between the

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[1] (a) Bartsch, R. A.; Zavada, J. *Chem. Rev.* **1980**, *80*, 454. (b) Bartsch, R. A. *Acc. Chem. Res.* **1975**, *8*, 128. (c) Ingold, C. K. *Structure and Mechanism in Organic Chemistry*, 2nd ed.; Cornell University Press: Ithaca, NY, 1969. (d) Saunders, W. H., Jr.; Cockerill, A. F. *Mechanisms of Elimination Reactions*; Wiley Interscience: New York, 1973; Chapter 1. (e) Saunders, W. H., Jr. *Acc. Chem. Res.* **1976**, *8*, 19. (f) Saunders, W. H., Jr. *The Chemistry of Alkenes*; Patai, S., Ed.; Wiley-Interscience: New York, 1964. (g) Baciocchi, E. *Acc. Chem. Res.* **1979**, *12*, 430. (h) Cordes, E. H.; Jencks, W. P. *J. Am. Chem. Soc.* **1963**, *85*, 2843. (i) Banthorpe, D. V. *Reaction Mechanisms in Organic Chemistry*. Vol. 2. *Elimination Reactions*; Hughes, E. D., Ed.; Elsevier: London, 1963. (j) Bunnett, J. F. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 225. (k) Bartsch, R. A.; Bunnett, J. F. *J. Am. Chem. Soc.* **1968**, *90*, 408. (l) Beltrame, P.; Biale, G.; Lloyd, D. J.; Parker, A. J.; Ruane, M.; Winstein, S. *J. Am. Chem. Soc.* **1972**, *94*, 2240. (m) Parker, A. J.; Ruane, M.; Palmer, D. A.; Winstein, S. *J. Am. Chem. Soc.* **1972**, *94*, 2228. (n) Cram, D. J.; Greene, F. D.; DePuy, C. H. *J. Am. Chem. Soc.* **1956**, *78*, 790. (o) Sicher, J. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 200. (p) Wolfe, S. *Acc. Chem. Res.* **1972**, *5*, 102. (q) DePuy, C. H.; Thurn, R. D.; Morris, G. F. *J. Am. Chem. Soc.* **1962**, *84*, 1314.

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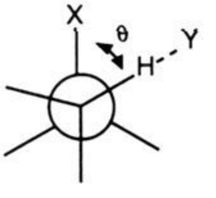
α and β carbons. As a result, there is essentially no double bond formation at the transition state of a true gauche elimination. After passing over the transition state barrier, rotation about the C_α–C_β axis leads to leaving group expulsion and double bond formation.



Gauche Transition State

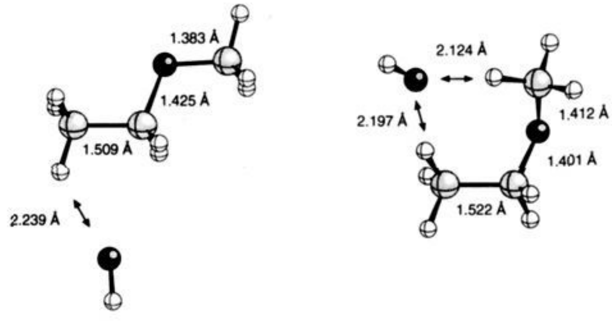
Ab initio studies are exceptionally useful for studying the conformational preferences of E2 eliminations because the calculations yield both the energy and the structure of the transition state.[2,3,6] To date, most theoretical studies have centered on reactions which give prototypical E2-type transition states where proton transfer, double bond formation, and leaving group expulsion occur synchronously. In early work, Bach et al.[2] studied the $E1_{cb}$-like reaction of H^- with CH_3CH_2F, but the transition state was not fully optimized and small basis sets were used. More recently, Dewar et al.[6c,d] have used the AM1 method to investigate a variety of E2 eliminations (some $E1_{cb}$-like), but for acyclic systems they only considered antiperiplanar transition states.

In an effort to study gas-phase, $E1_{cb}$-like eliminations, we have turned to the reactions of hydroxide with ethers. The gas-phase elimination reactions of ethers with strong bases have been the subject of several experimental studies, and rate constants as well as kinetic deuterium isotope effects have been reported for the reaction of HO^- with diethyl ether.[7,8] Because this system involves a strong base and a poor leaving group (an alkoxide), an $E1_{cb}$-like transition state is expected. The availability of experimental data as well as the simplicity of the ether/hydroxide systems makes them ideally suited for studying the structures and conformational preferences of $E1_{cb}$-like transition states. In this paper we present an ab initio study of the E2 elimination reaction of HO^- with $CH_3CH_2OCH_3$ to give H_2O, $CH_2{=}CH_2$, and CH_3O^-. Three pathways, anti- and synperiplanar as well as gauche, were investigated. In addition, ion–dipole encounter complexes were located. Finally, Bader's method for partitioning electron density was applied and integrated electron populations are reported.

Calculations

All calculations were carried out on a Multi-Flow-Trace14 computer using the GAUSSIAN 88 quantum mechanical package developed by Pople and co-workers.[9] All structures were fully optimized using basis sets derived from the standard 6-31G* basis.[10] When appropriate, the existence of multiple, stable rotamers was investigated. For anionic systems, diffuse sp orbitals were placed on all centers expected to bear a significant negative charge. In **1**, **2**, **3**, **4**, **5**, and HO^-, diffuse sp orbitals were placed on the oxygens and the β-carbon.[11] These basis sets will be designated as 6-31(+)G* in the text. Neutral systems were optimized with the standard 6-31G* basis set. The curvature of the potential energy surface at all minima and transition states was confirmed with analytical second derivatives, and frequencies are reported in the supplementary material. For energy comparisons, single-point calculations were done on the optimized geometries using a basis set that included polarization (p) functions on the hydrogens, 6-31(+)G**.[12] To correct for correlation effects, frozen-core Moeller–Plesset perturbation theory was applied up to the second level (MP2).[13] Energies also are corrected for zero-point energy differences (scaled by 0.9).[14]

Integrated electron populations and critical point densities were calculated using Bader's PROAIM package modified to run on a Sun 4/110 workstation. The details of these calculations have been described elsewhere.[3,15]



1 2

Figure 1. Optimized structures (6-31(+)G*) for ion–dipole complexes **1** and **2** (oxygen, dark shading; carbon, light shading; hydrogen, no shading).

Table I. Energies of Structures^a

structure	6-31(+)G* HF	6-31(+)G** HF	6-31(+)G** MP2	6-31(+)G* zero pt^b
1	−268.500 17 (−8.6)	−268.520 33 (−8.8)	−269.366 89 (−10.8)	71.6
2	−268.502 23 (−9.6)	−268.522 63 (−10.0)	−269.370 81 (−13.0)	71.9
3	−268.467 90 (+8.2)	−268.491 75 (+5.7)	−269.345 82 (−1.0)	68.2^c
4	−268.457 95 (+14.5)	−268.481 34 (+12.2)	−269.336 73 (+4.7)	68.2^d
5	−268.460 94 (+12.6)	−268.484 78 (+10.1)	−269.337 53 (+4.2)	68.2^e
$CH_3CH_2OCH_3$	−193.108 89	−193.121 23	−193.746 74	65.8^f
HO^-	−75.376 42	−75.383 93	−75.601 81	5.1

^{a} Energies in hartrees. Energies relative to separated reactants (corrected for zero-point vibrations) given in parentheses. ^{b} Zero-point vibrational energies scaled by 0.9. ^{c} For (HO^- $DCH_2CH_2OCH_3$), 67.0 kcal/mol, and for (HO^- $DCD_2CD_2OCH_3$), 59.4 kcal/mol. ^{d} Structure **4** has two imaginary frequencies and both are neglected in this calculation. ^{e} For (HO^- $DCH_2CH_2OCH_3$), 67.1 kcal/mol, and for (HO^- $DCD_2CD_2OCH_3$), 59.5 kcal/mol. ^{f} For $DCH_2CH_2OCH_3$, 63.9 kcal/mol, and for $CD_3CD_2OCH_3$, 55.9 kcal/mol.

Results

Ion–Dipole Complexes. In gas-phase ion–molecule reactions, the first minimum on the reaction coordinate is usually a weakly bound, ion–dipole complex. For HO^- + $CH_3CH_2OCH_3$, a number of ion–dipole complexes are possible, but only complexes related to E2 transition states were investigated. Two hydrogen-bonded

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[6] (a) Minato, T.; Yamabe, S. *J. Am. Chem. Soc.* **1988**, *110*, 4586. (b) Minato, T.; Yamabe, S. *J. Am. Chem. Soc.* **1985**, *107*, 4621. (c) Dewar, M. J.; Yuan, Y.-C. *J. Am. Chem. Soc.* **1990**, *112*, 2088. (d) Dewar, M. J.; Yuan, Y.-C. *J. Am. Chem. Soc.* **1990**, *112*, 2095. (e) Pross, A.; Shaik, S. S. *J. Am. Chem. Soc.* **1982**, *104*, 187.

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[8] de Koning, L. J.; Nibbering, N. M. M. *J. Am. Chem. Soc.* **1987**, *109*, 1715.

[9] *GAUSSIAN 88*: Frisch, M. J.; Head-Gordon, M.; Schlegel, H. B.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; DeFrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Fleuder, E. M.; Topiol, S.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA.

[10] A set of 6 d-functions were used: (a) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (b) Dill, J. D.; Pople, J. A. *J. Chem. Phys.* **1975**, *62*, 2921. (c) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

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[12] For a full discussion of these basis sets, see: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986 and references therein.

[13] DeFrees, D. J.; Levi, B. A.; Pollack, S. K.; Hehre, W. J.; Binkley, J. S.; Pople, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 4085.

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[15] For recent descriptions, see: (a) Bader, R. F. W. *Acc. Chem. Res.* **1985**, *18*, 9. (b) Bader, R. F. W.; Nguyen-Dang, T. T. *Adv. Quantum Chem.* **1981**, *14*, 63. (c) Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 985.

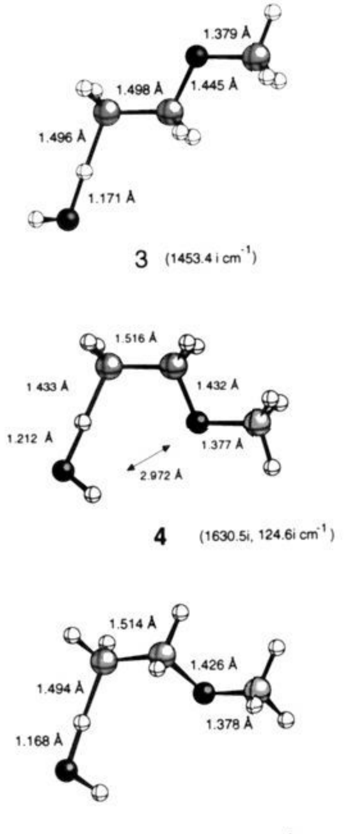

Figure 2. Optimized structures (6-31(+)G*) for transition states **3**, **4**, and **5** (oxygen, dark shading; carbon, light shading; hydrogen, no shading). Imaginary frequencies are given parenthetically.

ion–dipole complexes were located on the potential energy surface (Figure 1). Both are true minima (no imaginary frequencies) and involve hydrogens on the β-carbon (one anti (**1**) and the other gauche (**2**) to the $-OCH_3$ group). In **1**, the structure maintains C_s symmetry and the hydroxide oxygen is directly behind the C_α–OCH_3 bond. The HO–H_β distance is long (2.239 Å) in this complex and the geometry of the $CH_3CH_2OCH_3$ is hardly perturbed with the biggest difference occurring in the C_α–OCH_3 bond (0.03 Å extension). In complex **2**, the hydroxide interacts with a gauche hydrogen as well as a hydrogen on the OCH_3 group (O–H distances of 2.197 Å and 2.124 Å, respectively). At the MP2/6-31(+)G**//HF/6-31(+)G* level (Table I), the complexation energies for the formation of **1** and **2** are −10.8 and −13.0 kcal/mol, respectively. These values are typical of ion–dipole complexes,[16] and the greater stability of **2** can be rationalized by the availability of a second hydrogen bonding site.

E2 Transition State (Antiperiplanar). Using a 6-31(+)G* basis set, the transition state for the HO^- induced, antiperiplanar elimination of $CH_3CH_2OCH_3$ was located (**3**). Analysis of the analytical second-derivative matrix leads to a single imaginary frequency whose normal mode mainly corresponds to the C_β–H_β stretch. The structure (Figure 2) exhibits nearly perfect periplanarity in the H_β–C_β–C_α–OCH_3 framework (dihedral angle = 180.26°) although the hydroxy hydrogen is significantly twisted out of the plane (H–O–H_β–C_β dihedral = 128°) and C_s symmetry is not observed. As expected, the transition state has an $E1_{cb}$-like structure. The C_β–H_β bond length (1.496 Å) is exceptionally long and the HO–H_β bond length (1.171 Å) is relatively short. Although proton transfer is nearly complete at the transition state, little double bond formation or leaving group expulsion has occurred. The C–C bond has contracted only 0.011 Å and the C_α–OCH_3 bond has lengthened 0.020 Å relative to complex **1**. In addition, there has been little change in the hybridization of the carbon framework. As has been noted before for E2 eliminations,[3] the proton transfer involves a nearly linear arrangement of the base, H_β, and C_β. At the MP2/6-31(+)G**//HF/6-31-(+)G* level, the energy of this transition state is −1.0 kcal/mol relative to the separated reactants (Table I).[17]

Table II. Integrated Atomic Populations[a]

structure	element	n[b]	net charge	Mulliken charges
3	HO[c]	9.83	−0.83	−0.69
	H_β	0.42	+0.58	+0.48
	C_β	6.21	−0.21	−0.92
	CH_3O[c]	17.69	−0.69	−0.34
5	HO[c]	9.82	−0.82	−0.70
	H_β	0.39	+0.61	+0.51
	C_β	6.20	−0.20	−0.90
	CH_3O[c]	17.69	−0.69	−0.33
$CH_3CH_2OCH_3$	H_β	1.08	−0.08	+0.12
	C_β	5.75	+0.25	−0.43
	CH_3O[c]	17.59	−0.59	−0.27

[a] Wave functions generated with 6-31(+)G** or 6-31G** basis set. [b] Integrated population from volumes defined with the Bader procedure. [c] Sum of populations on given atoms.

E2 Transition State (Synperiplanar). All attempts to locate a synperiplanar transition state for the reaction of HO^- with $CH_3CH_2OCH_3$ led to structures with two or more imaginary frequencies. A synperiplanar transition state was optimized within C_s symmetry constraints, **4**, and was found to be a second-order saddle point with one imaginary frequency corresponding to the H_β–C_β stretch and the other to a rotation about the C_β–C_α bond axis. Consequently, a synperiplanar transition state is not present on the Hartree–Fock potential energy surface for this elimination.

E2 Transition State (Gauche). The absence of a synperiplanar transition state led us to investigate other C_α–C_β rotamers as possible E2 transition states. A gauche transition state with a staggered conformation (**5**) was located (Figure 2). The imaginary frequency (1270i cm^{-1}) in this structure corresponds to the H_β–C_β stretch with a minor contribution from C_α–C_β rotation. As in **3**, the structure is best characterized as $E1_{cb}$-like and contains a long C_β–H_β distance (1.494 Å) and short HO–H_β distance (1.168 Å). The C–C bond exhibits almost no contraction (0.008 Å relative to **2**) and the C_α–OCH_3 bond is only slightly elongated (0.025 Å relative to **2**). Remarkably, the structure is nearly perfectly staggered (H_β–C_β–C_α–OCH_3 dihedral = 56.86°) with almost no preference for overlap between the H_β and OCH_3. A nearly linear proton transfer geometry also is seen in **5**. At the MP2/6-31-(+)G**//HF/6-31(+)G* level, the energy of the gauche transition state is +4.2 kcal/mol relative to the separated reactants (Table I).

Electron Density Analysis. The calculation of atomic electron populations has proven to be very useful in characterizing the bonding of molecules.[3,15,18] It is a particularly valuable tool for studying reaction paths and transition states because it allows chemists to monitor the shifts in electron density that occur during a chemical transformation and correlate them with the changes in geometry. Although all population analyses require an arbitrarily chosen partitioning scheme, the approach developed by Bader and co-workers is rigorously defined and based on the intuitive assumption that density near an atom should be associated with that atom.[15] Because Bader's method involves a partitioning

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(16) Su, T.; Bowers, M. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. I.

(17) Moeller–Plesset (MP) corrections have a significant effect on the energies of the transition states relative to the separated reactants; however, MP corrections do not substantially affect the order of stabilities of the transition states.

(18) For example, see: (a) Bachrach, S. M.; Streitweiser, A., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 2283. (b) Bachrach, S. M.; Streitweiser, A., Jr. *J. Comput. Chem.* **1989**, *10*, 514. (c) Gronert, S.; Glaser, R.; Streitweiser, A., Jr. *J. Am. Chem. Soc.* **1989**, *111*, 3111. (d) Bader, R. F. W.; Duke, A. J.; Messer, R. R. *J. Am. Chem. Soc.* **1973**, *95*, 7715. (e) Reed, A. E.; Weinhold, F. *J. Am. Chem. Soc.* **1986**, *108*, 3586. (f) Reed, A. E.; Weinhold, F. *J. Am. Chem. Soc.* **1985**, *107*, 1919.

in space (integrated population), it is less basis set dependent than orbital partitionings (Mulliken populations).[18] Although Bader's method has been widely accepted, it recently was criticized in the literature.[19] The criticisms neglect the fact that, unlike other population schemes, a Bader population is physically meaningful; it is the integrated population within a defined volume (the virial surface). The way in which these populations are interpreted may be questioned, but the population values are valid within the given level of theory. Of course, in covalent systems, charges derived from electron density analysis are simply evidence of bond polarization. The charges highlight the importance of ionic resonance forms, but do not imply that the bond is purely ionic (lacking shared density).

The substrate, $CH_3CH_2OCH_3$, as well as transition states **3** and **5** were subjected to electron density analysis with a modified version of Bader's PROAIM package (Table II).[15] For this analysis, the populations on the leaving group (CH_3O), β-carbon, β-hydrogen, and base (HO^-) can be used to gauge the shifts in electron density in going from reactants to the transition states. In $CH_3CH_2OCH_3$ (Table II), the C_α–OCH_3 bond is significantly polarized with the methoxy group having excess density and an integrated population of 17.59 electrons (charge = −0.59). Because the C–H bond densities are slightly polarized toward hydrogen, a small electron deficiency on C_β (pop. = 5.75) and surplus on H_β (pop. = 1.08) are observed.

The $E1_{cb}$-like nature of the antiperiplanar transition state, **3**, is confirmed by the population study. In going from the reactants to the transition state, the leaving group (CH_3O) experiences only a small population increase (17.59 ⇒ 17.69 electrons), whereas the C_β population increases dramatically (5.75 ⇒ 6.21 electrons). As expected for an $E1_{cb}$-like transition state, H_β has significant protic character (pop. = 0.42 electron). For comparison, the hydrogens in H_2O have integrated populations of 0.38 electron at the 6-31G** level. A more reliable measure of the extent of proton transfer is the charge on the HO–H_β fragment. The HO–H_β fragment has a charge of −1.08 (−1.00 + −0.08) in the reactants and 0.00, of course, in the product, H_2O. In transition state **3**, the HO–H_β fragment charge is −0.25 or approximately 25% of the value found in the reactants.

The integrated populations for the gauche transition state, **5**, are also listed in Table II and are very similar to those found for the antiperiplanar transition state (the greatest deviation is 0.03 electron). This suggests that the bonding patterns in the two transition states are closely related. Mulliken populations for the substrate and the transition states are listed in Table II for comparison. Although the absolute values differ considerably (Mulliken populations overestimate the charge on C_β and underestimate it on CH_3O), similar trends are observed, and an $E1_{cb}$-like transition state is indicated.

Further confirmation of the $E1_{cb}$-like character of the transition states can be found by analyzing the electron densities of the bond critical points (the point of minimum density along the bond axis). Bader and others[20] have shown that critical point densities (ρ) give a reasonable measure of the relative strengths or orders of covalent bonds.[21] Absolute values of ρ are dependent on a number of factors including the nature and size of the bonding atoms; however, relative values reflect the amount of shared density and therefore the strength of the covalent interaction.

The relatively large ρ value for the C_α–OCH_3 bond in transition state **3** (0.228 compared to 0.266 in $CH_3CH_2OCH_3$) indicates that leaving group expulsion has hardly begun at the transition state (Table III). For comparison, in our earlier study of F^- + CH_3CH_2Cl (a predominantly E2H system),[3] the ρ value for the C_α–Cl bond is reduced by over 60% at the transition state. The extent of proton transfer in **3** is demonstrated by the C_β–H_β ρ values. At the transition state, the ρ value for the C_β–H_β bond (0.104) is less than 40% of the value found in the substrate, $CH_3CH_2OCH_3$ (0.286). Because π-bond formation occurs off-axis, the ρ value for the C_α–C_β bond is not very sensitive to the extent of π bonding. Nonetheless, essentially no transition state increase is observed in the ρ value of the carbon–carbon bond. As in the population study, the values for the gauche transition state, **5**, mirror those found for the antiperiplanar one, **3**. However, subtle differences in the ρ values indicate that the gauche pathway involves a slightly more $E1_{cb}$-like transition state. In particular, a larger ρ value is found for the C_α–OCH_3 bond and a smaller one for the C_β–H_β bond.

Table III. Critical Point Densities[a]

structure	bond	ρ (e/au^3)
3	HO–H_β	0.176
	H_β–C_β	0.104
	C_β–C_α	0.265
	C_α–OCH_3	0.228
5	HO–H_β	0.193
	H_β–C_β	0.095
	C_β–C_α	0.258
	C_α–OCH_3	0.237
$CH_3CH_2OCH_3$	H_β–C_β	0.286
	C_β–C_α	0.266
	C_α–OCH_3	0.266

[a] Critical points derived with Bader approach using 6-31(+)G** and 6-31G* basis sets.

Discussion

As expected for the combination of a strong base and a weak leaving group, the elimination reaction of HO^- with $CH_3CH_2OCH_3$ has transition states with significant $E1_{cb}$-like character.[22] This is clearly evident in the transition state geometries, integrated populations, and critical point densities. The most surprising result from this study is the effect of $E1_{cb}$-like character on the preference for periplanarity. It has been assumed that because bimolecular eliminations involve π-bond formation, periplanarity is a critical requirement for the transition state. Indeed, a well-respected physical organic chemistry text states,[23] "E2 reactions, if they are to go at all well, require that H and X be either syn or anti periplanar in the transition state". However, in this study, a syn–gauche transition state is more stable than a synperiplanar transition state (antiperiplanar is most stable). Obviously, periplanarity is an important, but not a necessary component of the transition states of 1,2 eliminations.

The conformational preferences of bimolecular elimination reactions can be partitioned into two important interactions, conjugation and steric hindrance. A clear advantage of a periplanar transition state is the ability of the developing carbon lone pair to hyperconjugate to the carbon-leaving group bond. In this way, the charge on the nucleophile can be smoothly transferred to the leaving group, and the transition state can be stabilized by the formation of a partial π-bond. The importance of this interaction is dependent on the ability of the developing carbon lone pair to interact with the σ* orbital of the carbon-leaving group bond. An inherent consequence of a poor leaving group is a high σ* energy and a weak hyperconjugative interaction. The small elongation of the C_α–OCH_3 bond in **3** is clear evidence that hyperconjugation is playing a minor role in the transition state of this $E1_{cb}$-like reaction.

The second factor affecting the preference for periplanarity involves the steric repulsions of the transition state conformation. An antiperiplanar transition state incorporates a staggered conformation and therefore avoids unfavorable eclipsing interactions. Consequently, an antiperiplanar transition state is favored by both conjugative and steric considerations and, therefore, is generally preferred for gas-phase E2 eliminations. In contrast, a synperiplanar transition state requires an eclipsed conformation about

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(19) Perrin, C. L. *J. Am. Chem. Soc.* **1991**, *113*, 2865.

(20) For example, see: (a) Knop, O.; Boyd, R. J.; Choi, S. C. *J. Am. Chem. Soc.* **1988**, *110*, 7299. (b) Bader, R. F. W.; Slee, T. S.; Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1983**, *105*, 5061.

(21) In the text, critical point densities are reported in units of e/au^3.

(22) Although the reactions have a high degree of $E1_{cb}$-like character, the eliminations are concerted. All attempts to find $E1_{cb}$ intermediates (H_2O –$CH_2CH_2OCH_3$ complexes) failed.

(23) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper & Row: New York, 1987.

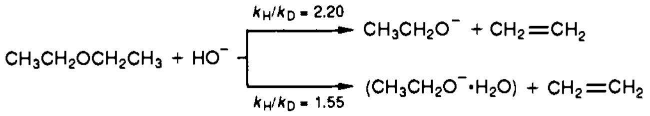
the C_α–C_β axis and consequently is destabilized by steric interactions.[24] As a result, the preference for a synperiplanar transition state is based on a balance between two counteracting effects, the advantage of conjugation and the disadvantage of an eclipsed conformation. In systems with a weak hyperconjugative interaction, steric effects dominate and gauche transition states result. The fact that the gauche transition state (**5**) is only 5.2 kcal/mol less stable than an antiperiplanar one (**3**) clearly indicates that hyperconjugation provides only a modest stabilization and that the inductive effect of the methoxy group must play an important role in stabilizing these transition states. Moreover, Bach[2] has pointed out that on the basis of orbital overlap considerations, hyperconjugation is less effective in the syn conformation of an E2 elimination. For example, in our studies of F^- and PH_2^- + CH_3CH_2Cl (E2H systems where double bond formation is significant in the transition state),[3] we found that synperiplanar transition states were considerably less stable than antiperiplanar transition states (by 12.4 and 8.7 kcal/mol, respectively). Given the minor stabilization provided by hyperconjugation in the antiperiplanar transition state of HO^- + $CH_3CH_2OCH_3$, it is not surprising that hyperconjugation in the synperiplanar conformation cannot provide enough stabilization to overcome the steric destabilization of an eclipsed conformation.

Although generally it has been assumed that E2 transition states must be periplanar, a gauche transition state is perfectly consistent with variable transition state theory.[1] Because the substrate prefers a staggered conformation, proton transfer will begin from either an anti (**1**) or gauche (**2**) conformation. From a gauche conformation, the reaction involves four concerted processes, proton transfer, C_α–C_β bond rotation (to give a planar alkene), double bond formation, and leaving group expulsion. These processes are not necessarily synchronous, and therefore in an $E1_{cb}$-like system, it is possible for proton transfer to precede C_α–C_β bond rotation and yield a transition state with a gauche conformation. In this case, C_α–C_β bond rotation, double bond formation, and leaving group expulsion occur after crossing the transition state barrier. With better leaving groups, C_α–C_β bond rotation occurs before the transition state is reached so that the system can take advantage of hyperconjugation and partial π-bond formation. As a result, the transition state adopts a synperiplanar conformation.

It must be noted that the energy difference between the synperiplanar and the gauche transition states is very small. At the HF/6-31(+)G**//HF/6-31(+)G* level it is 2.1 kcal/mol, and at the MP2/6-31(+)G**//HF/6-31(+)G* level it is only 0.5 kcal/mol. It is therefore possible that at higher levels of theory the synperiplanar transition state will be favored. The remarkable result of this study, however, is the insensitivity of the transition state barrier to the torsional angle (H_β–C_β–C_α–X). For a 120° range of torsional angles (from gauche, $\theta = 60°$ to gauche, $\theta = -60°$), the transition state barrier varies by only 2 kcal/mol at the Hartree–Fock level. *In $E1_{cb}$-like reactions, the barrier to syn eliminations (gauche and synperiplanar transition states give the same stereochemical results) is virtually independent of the torsional angle.* Consequently, $E1_{cb}$-like systems that are constrained to non-periplanar transition states (ring systems) should not face unusually large barriers to syn eliminations.[25] In more highly substituted $E1_{cb}$-like systems (e.g., $(CH_3)_2CHCH_2OCH_3$), gauche transition states should be much more favorable than synperiplanar ones because the increased steric repulsions will disfavor an eclipsed (synperiplanar) conformation.

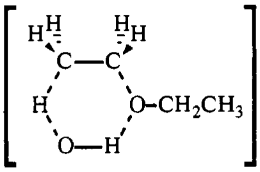
Comparison to Gas-Phase Experiments. In separate studies, DePuy[7] and Nibbering[8] have investigated the gas-phase reactions of strong bases with aliphatic ethers. Because HO^- does not react with CH_3OCH_3 to give CH_3O^-, DePuy and Bierbaum[7a] concluded that although the S_N2 channel is exothermic, it is not active in the reactions of HO^- with ethers. When HO^- is allowed to react with $CH_3CH_2OCH_2CH_3$ in the gas phase, two elimination products are observed, $CH_3CH_2O^-$ and $(CH_3CH_2O^-{\cdot}H_2O)$.[26] The reaction is relatively fast (5.8×10^{-10} cm^3 s^{-1}) and has an efficiency of 0.26.[7c] The efficiency is the measured rate divided by the calculated collision rate. In gas-phase ion–molecule reactions, the initially formed collision complex can either pass over the transition state barrier to give products or dissociate back to reactants. Because the dissociation pathway is usually favored by entropy (it is much less ordered than a reaction transition state), only reactions with negative or very small, positive activation barriers are observed under typical gas-phase conditions. Although quantitative correlations of gas-phase reaction rates with transition state barriers are complicated,[7c,27] an efficiency of 0.26 is consistent with a slightly negative activation barrier. Moreover, Bierbaum and Bowers have used statistical rate theory and an idealized transition state model to estimate a transition state barrier of about −4.6 kcal/mol for the reaction of HO^- with $CH_3CH_2OCH_2CH_3$.[7c] Given the uncertainties of their model, this value is in reasonable accord with our calculated barrier (−1 kcal/mol) for the reaction of HO^- with $CH_3CH_2OCH_3$ (antiperiplanar). In addition, since the elimination reactions of ethyl methyl ether are less exothermic than those with diethyl ether, a slightly larger transition state barrier is anticipated.[28]

Two studies have focused on the deuterium isotope effects in the reaction of HO^- with $CH_3CH_2OCH_2CH_3$.[7c,8] In a thorough gas-phase study, de Koning and Nibbering[8] found that different primary kinetic isotope effects are operative in the formation of the free ethoxide and the ethoxide–water complex.[29]



They interpreted these results as evidence of two competing mechanisms, one involving an antiperiplanar transition state and leading to the free $CH_3CH_2O^-$ and the other involving a synperiplanar transition state and yielding the solvate $(CH_3CH_2O^-{\cdot}H_2O)$.

This rationalization was based on the assumption that a cyclic transition state, **6**, was possible for the syn elimination. However,



6

this interpretation is not consistent with our theoretical studies of HO^- + $CH_3CH_2OCH_3$. In this reaction, neither synperiplanar nor cyclic transition states could be found on the potential energy surface.[30] Cyclic transition states of this type require an eclipsed conformation and an unfavorable, bent proton transfer geometry.[31]

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(24) Lowe, J. P. *Prog. Phys. Org. Chem.* **1968**, *6*, 1.

(25) Using the AM1 method, Dewar has found relatively small energy differences between transition states constrained by rings to be gauche and synperiplanar. See ref 6d.

(26) Solvates are common products in gas-phase eliminations. For example, see: Ridge, D. P.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 3595.

(27) For sample dynamics studies of gas-phase ion–molecule reactions, see: (a) Olmstead, W. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 4219. (b) Pellerite, M. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1983**, *105*, 2672. (c) Tucker, S. C.; Truhlar, D. G. *J. Am. Chem. Soc.* **1990**, *112*, 3338. (d) Tucker, S. C.; Truhlar, D. G. *J. Phys. Chem.* **1989**, *93*, 8138. (e) Chesnavich, W. J.; Bass, L.; Su, T.; Bowers, M. T. *J. Chem. Phys.* **1981**, *74*, 2228.

(28) The β-elimination of $CH_3CH_2OCH_3$ ($\Delta H° = +6.2$ kcal/mol) is 2.5 kcal/mol less exothermic than the β-elimination of $CH_3CH_2OCH_2CH_3$ ($\Delta H° = +3.7$ kcal/mol): (a) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. No. 1. (b) Stull, D. R.; Westrun, E. F.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*, John Wiley: New York, 1969.

(29) To determine the isotope effects, de Koning and Nibbering studied the reactions of $CD_3CH_2OCH_2CH_3$, $CD_3CD_2OCH_2CH_3$, and $CD_3CD_2OCD_2CD_3$ (see ref 8).

(30) Several attempts were made to find a cyclic transition state structure such as 6. In each case, multiple negative eigenvalues were found. Moreover, systems constrained to be periplanar relaxed to structure 4.

It is possible that even though the gauche transition state (**5**) does not involve intramolecular hydrogen bonding, it may preferentially lead to the solvate ($CH_3CH_2O^-\cdot H_2O$); however, the experimental studies indicate that the ethoxide–water complex is the major product,[7c,8] whereas the theoretical studies predict that the gauche elimination should have a significantly larger barrier (5.2 kcal/mol) than the antiperiplanar elimination. Additional evidence against competing pathways is found in the calculated vibrational frequencies. On the basis of zero-point energy differences, the calculations predict that the barriers for both the antiperiplanar and gauche eliminations of $CD_3CD_2OCH_3$ are about 1.1 kcal/mol above those of $CH_3CH_2OCH_3$, and therefore both pathways should give similar kinetic isotope effects.[32,33] Our calculated differences in transition state barriers are in good accord with Bierbaum and Bowers' earlier estimate.[7c] Using their statistical rate model and the observed kinetic isotope effects, they predicted that the barrier in $CD_3CD_2OCD_2CD_3$ is 1.1 kcal/mol greater than that in $CH_3CH_2OCH_2CH_3$. Given the present theoretical results, it seems unlikely that a cyclic transition state is involved in the gas-phase reactions of HO^- with ethers, and therefore another explanation must be found for the different isotope effects observed in the two product channels. Although it is not completely consistent with the energy dependence that de Koning and Nibbering reported,[8] a rational explanation is that the reaction involves only an antiperiplanar pathway[34] and that a second isotope effect is active in the partitioning between solvated and unsolvated products.

Conclusions

For β-elimination reactions with a high degree of $E1_{cb}$-like character, the preference for periplanarity is greatly reduced. Because the carbon-leaving group bond is hardly broken in the transition state, there is little advantage to hyperconjugation and partial π-bond formation. As a result, steric effects can become important in determining the preferred conformation. Synperiplanar transition states are only possible when the advantage of conjugation outweighs the steric disadvantages of an eclipsed conformation. In $E1_{cb}$-like reactions, this is not necessarily true and gauche transition states are possible. These effects are almost perfectly balanced in the reaction of HO^- with $CH_3CH_2OCH_3$ where a gauche transition state is slightly more stable than a synperiplanar transition state. This highlights the fact that in $E1_{cb}$-like syn eliminations, the transition state barrier is relatively insensitive to the torsional angle (H_β–C_β–C_α–X). However, antiperiplanar transition states generally are preferred for gas-phase β-eliminations because they allow for conjugation within a staggered conformation. Further studies on the effect of substitution in E2 transition states have been completed and will be published subsequently.[35]

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Registry No. Hydroxide, 14280-30-9; ethyl methyl ether, 540-67-0.

Supplementary Material Available: Listing of *Z*-matrix elements, energies, frequencies, and reaction coordinates (10 pages). Ordering information is given on any current masthead page.

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(31) In all previous theoretical studies of E2 eliminations, nearly linear proton transfer geometries (base–H_β–C_β) have been observed (see ref 2, 3, 6).

(32) The zero-point-energy differences predict a smaller isotope effect for the antiperiplanar and gauche eliminations of the (HO^-–$DCH_2CH_2OCH_3$) system (a transition state barrier difference of about 0.8 kcal/mol compared to the all hydrogen substrate). Therefore, both primary and secondary isotope effects are important in these reactions. Experimentally, de Koning and Nibbering have noted this result; see ref 8.

(33) Attempts to analyze the theoretical results with a simple RRKM dynamics approach (see ref 27a) led to unrealistically low rates and exceptionally large k_H/k_D values. Undoubtedly these errors result from treating low-frequency vibrations as harmonic oscillators rather than as hindered rotors (the differences cannot be explained solely on the basis of errors in the calculated barrier). Although beyond the scope of the present study, a more sophisticated dynamics treatment is appropriate for a system that is characterized by many low-frequency vibrations and the possibility of tunnelling (see ref 27c–e).

(34) Although entropy may slightly favor the gauche elimination (the small torsional barrier and the presence of two gauche pathways should increase the entropy), the large difference in activation energy (5.2 kcal/mol) should ensure that antiperiplanar eliminations dominate.

(35) Syn–gauche transition states have been observed in other systems, and the borderline between synperiplanar and syn-gauche transition states has been investigated: Gronert, S. Manuscript in preparation.

Ab Initio Calculations on Silicon Analogues of the Allyl Radical

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Abstract: Calculations at the CI-SD/6-31G* level of theory have been performed in order to determine the effect on the A–H bond dissociation energy (BDE) in $X\text{–}AH_3$ (A = C and A = Si) of replacing X = H_3C– by X = $H_2C{=}CH$– and $H_2Si{=}CH$– and of replacing X = H_3Si– by X = $H_2C{=}SiH$– and $H_2Si{=}SiH$–. The conjugative stabilization energies (CSEs) of the resulting allylic radicals have been obtained from the energies calculated to be required to twist a terminal $AH_2^\bullet$ group out of conjugation. Except for X = $H_2C{=}CH$– and $H_2Si{=}CH$– in $X\text{–}CH_2^\bullet$, these two definitions of allylic resonance energy give nearly identical values. The reason for the calculated difference between $-\Delta$BDE and CSE in $H_2C{=}CH\text{–}CH_2^\bullet$ and in $H_2Si{=}CH\text{–}CH_2^\bullet$ is discussed. It is also found that, with the exception of $H_2Si{=}CH\text{–}SiH_2^\bullet$, the calculated allylic resonance energies are generally those expected from the π BDEs in $H_2C{=}CH_2$, $H_2C{=}SiH_2$, and $H_2Si{=}SiH_2$. It is shown that pyramidalization at silicon lowers the resonance energy of $H_2Si{=}CH\text{–}SiH_2^\bullet$ from that expected, based on the strength of the C–Si π bond in $H_2C{=}SiH_2$.

The results of ab initio calculations show that substituents, X, affect the A–H bond dissociation energy (BDE) of $X\text{–}AH_3$ differently, depending on whether A is carbon or silicon.[1] For A = C, as well as for A = Si, X groups that can delocalize the unpaired electron in the $X\text{–}AH_2^\bullet$ radical tend to lower the A–H BDE. However, since carbon forms stronger π bonds than silicon,[2] conjugative stabilization of the radical formed by breaking the A–H bond is generally found to be more important for A = C than for A = Si.

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(1) Coolidge, M. B.; Borden, W. T. *J. Am. Chem. Soc.* **1988**, *110*, 2298.

(2) Review: Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272.