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Theoretical Transition Structures for Radical Additions to Alkenes

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Transition structures for the additions of $H^{\bullet}$, $CH_3^{\bullet}$, $CH_3CH_2^{\bullet}$, $HO^{\bullet}$, and $H_2C{=}CH^{\bullet}$ to ethylene, $H^{\bullet}$, $CH_3^{\bullet}$, $CH_3CH_2^{\bullet}$, $HO^{\bullet}$, and $CH_3O^{\bullet}$ to propene, and $CH_3^{\bullet}$ to 2-methylpropene have been located with ab initio UHF theory and the 3-21G basis set. The results are compared to previous literature results, carried out at these and higher ab initio levels, and to several semiempirical calculations. Variations in angles of radical attack upon substitution, substituent effects on rates and orientation, and the preferred conformations of alkyl groups in the transition structures are discussed. The results are used to develop a force-field for radical additions.

For several years, we have investigated (1) attack angles of reagents and conformations of allylic substituents in transition structures for additions to unsaturated systems,[2] (2) the factors controlling the competition between addition and hydrogen abstraction in reactions of radicals with alkylethylenes,[3] and (3) the development of force-field models to rationalize and predict the regioselectivities and stereoselectivities of intramolecular radical additions.[4] These interests have led us to undertake the study of transition structures of a variety of radical addition reactions. We report here our results to date. These are relevant to the understanding of radical attack angles in addition reactions, conformational preferences in transition structures, stereoselectivity in radical cyclizations,[4,5] and regioselectivity in radical additions.[6,7] We have also used these results to parameterize a force-field for prediction of intramolecular radical addition regioselectivities and stereoselectivities.[4] We compare our results to previous calculations at many levels, which have been reviewed recently by Lefour et al.[7] Earlier studies include ab initio calculations on additions of $H^{\bullet}$,[7,8] $CH_3^{\bullet}$,[9] and $HO^{\bullet}$ [10] to ethylene, Schlegel's higher level calculations of $H^{\bullet}$, $F^{\bullet}$, and $Cl^{\bullet}$ additions to ethylene[11] and $H^{\bullet}$ additions to fluoroethylene and chloroethylene,[12] $H^{\bullet}$ additions to vinylamine and vinylborane,[7] as well as MINDO/3 studies of methyl radical additions to ethylene and propene,[13,14] vinyl and cyclopropyl radical additions to ethylene,[15,16] and MNDO studies of the addition of vinyl to radical to ethylene.[17] Earlier calculations are referred to in these papers.[7-17]

Programs, Methods, and Results

All calculations on radicals were carried out at the ab initio unrestricted Hartree–Fock (UHF) level,[18] using the 3-21G basis set,[19] and either the GAUSSIAN 80 and GAUSSIAN 82 series of programs created by Pople and co-workers[20] or the IMSPACK programs of Morokuma and co-workers.[21] Restricted Hartree–Fock (RHF) theory was used for closed-shell systems. These programs include gradient optimization procedures for locating transition structures using first and second derivatives. In one case, a transition structure was located separately with the somewhat superior 4-31G basis set.[22] Schlegel's 6-31G* transition structures provide higher level comparisons[10-12] and establish the qualitative validity of the results obtained with smaller basis sets. Frequency calculations were carried out for hydrogen atom, methyl radical, and hydroxyl radical additions to ethylene, in order to verify that these stationary points are authentic transition structures possessing only one imaginary harmonic vibrational frequency, associated with the negative force constant for motion along the reaction coordinate. In all other cases, stationary points which are energy maxima with respect to the forming bond length and have only one negative eigenvalue in the approximate Hessian matrix were found, but the full frequency calculations were not performed.

The 3-21G transition structures for the additions of $H^{\bullet}$, $CH_3^{\bullet}$, $CH_3CH_2^{\bullet}$ (gauche and anti), $H_2C{=}CH^{\bullet}$, and $HO^{\bullet}$ to

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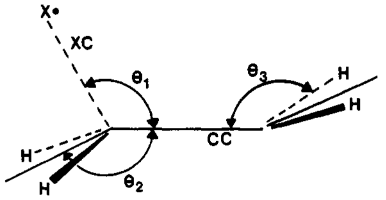
Table I. Geometries and Energies of Transition Structures for Radical Additions to Ethylene



	radical							
	H•	H•	CH_3•	CH_3CH_2•	CH_3CH_2•	CH_2═CH•	HO•[c]	HO•[c]
basis set	3-21G	4-31G	3-21G	3-21G	3-21G	3-21G	3-21G	6-31G*
symmetry	C_s	C_s	C_s	C_1 (gauche)	C_s (gauche)	C_s (0°)	C_s	C_s
XC(A)[b]	2.018	2.015	2.269	2.252	2.254	2.315	1.900	1.900
CC(A)	1.354	1.357	1.375	1.376	1.376	1.367	1.395	1.400
θ_1, deg	105.9	106.2	107.8	108.5	108.6	106.9	104.5	106.4
θ_2, deg	170.9	170.5	161.6	160.7	161.6	164.1	155.8	154.0
θ_3, deg	178.1	178.1	176.3	176.5	176.3	177.1	176.4	174.3
E, au	−79.09357		−116.93288	−155.75349	−155.75345	−154.55719	−155.55606	
E_{rel}[a]	2.3	2.2[d]	6.7	7.0	7.0	4.1	5.3	8.7

[a] Energy of TS relative to the energy of radical (UHF) plus alkene (RHF), in kcal/mol. [b] X is the bisector of the HCH angle. [c] From ref 10. [d] From ref 8.

Table II. Geometries and Energies of 3-21G Transition Structures for Additions of H• and CH_3• to Propene and CH_3• to 2-Methylpropene (Isobutene)

	radical					
	H•	H•	CH_3•	CH_3•	CH_3•	CH_3•
alkene	propene	propene	propene	propene	isobutene	isobutene
site of attack	C_1	C_2	C_1	C_2	C_1	C_2
XC, Å	2.008	1.957	2.266	2.262	2.266	2.270
CC, Å	1.353	1.359	1.375	1.379	1.376	1.382
θ_1, deg	105.8	101.5	107.8	104.2	107.6	101.5
θ_2, deg	170.6	167.1	161.0	158.8	160.8	155.7
θ_3, deg	177.6	177.3	174.9	175.5	173.9	174.8
E, au	−116.91623	−116.91361	−155.75491	−155.75202	−194.57746	−194.57149
E_{rel}, kcal/mol	2.5	4.1	7.3	9.2	7.7	11.5
ΔE_{rel}	1.6		1.9		3.8	

Table III. Geometries and Energies of Transition Structures for Addition of Ethyl Radical to C_1 of Propene[a]

	TS1	TS2	TS3
XC, Å	2.246	2.245	2.243
CC, Å	1.380	1.381	1.381
θ_1, deg	105.4	104.8	104.7
θ_2, deg	157.7	157.2	157.4
θ_3, deg	175.7	175.6	175.4
θ_4,[b] deg	176.9	−67.7	−81.6
θ_5,[b] deg	51.8	58.0	153.1
E, au	−194.57274	−194.57216	−194.57208
E_{rel} kcal/mol	9.4	9.7	9.7
ΔE_{rel}	0	0.37	0.41

[a] Geometry definitions as in Table I. [b] θ_4 is the $(H_3)CCCC(H_3)$ dihedral angle; θ_5 is the $(H_3)CCC{=}C$ dihedral angle.

ethylene are shown in Figure 1, and salient geometrical features and energetics are given in Table I.[24] The transition structures for the additions of H• and CH_3• to propene in both orientations, and of CH_3• to 2-methyl-2-butene in both orientations are shown in Figure 2, and geometrical details are given in Table II. The transition structures for CH_3CH_2• addition to C_2 of propene are shown in Figure 3 and are summarized in Table III.

Table IV. Geometries and Energies of Transition Structures for Additions of HO• and CH_3O• to C_1 of Propene

	radical	
	HO•	CH_3O•
XC, Å	1.937	1.886
CC, Å	1.393	1.395
θ_1, deg	103.3	108.2
θ_2, deg	153.2	153.4
θ_3, deg	169.8	172.5
E, au	−191.37907	−230.19796
E_{rel}, kcal/mol	5.3	11.3

Transition structures for HO• and CH_3O• additions to C_1 of propene are shown in Figure 4, and geometrical details and energetics are given in Table IV.[23] For the addition of HO• to ethylene, we also located a stationary point with C_s symmetry and HOCC = 180°. This stationary point proved to have two negative eigenvalues in the force constant matrix, so this is actually a transition structure for rotation of the C_s transition structure with HOCC = 0°, shown in Figure 3. Schlegel has also located this transition structure.[10] The methoxy radical addition transition structure, shown in Figure 3, has the CO bond located gauche to the alkene CC bond, whereas the corresponding anti structure is a second-order saddle point. Two staggered transition structures are found for ethyl radical addition to ethylene, and three are found for the addition of ethyl radical to C_2 of propene. These are discussed in detail below.

Discussion

Activation Energies. The activation energies listed in Tables I–IV are of the same order of magnitude as those

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[24] (a) Experimental activation energies from many different studies have been complied in: *CRC Handbook of Bimolecular and Termolecular Gas Reactions*; Kerr, J. A., Moss, S. J., Eds.; CRC: Boca Raton, FL, 1981. Ranges of experimental activation energies listed there are: H• + ethylene, 0.7–4.0 kcal/mol; H• + propene C_1, 1.2–1.7 kcal/mol; H• + propene C_2, 2.8–2.9 kcal/mol; Me• + ethylene, 6.8–6.9 kcal/mol; Me• + propene C_1, 7.1 kcal/mol; Et• + ethylene, 5.5–8.6 kcal/mol; HO• + ethylene, −0.9–6.4 kcal/mol. (b) The most recent experimental measurement gives E_a = −0.7 kcal/mol for the HO• + ethylene reaction: Zellner, R.; Lorenz, K. *J. Phys. Chem.* **1984**, *88*, 984.

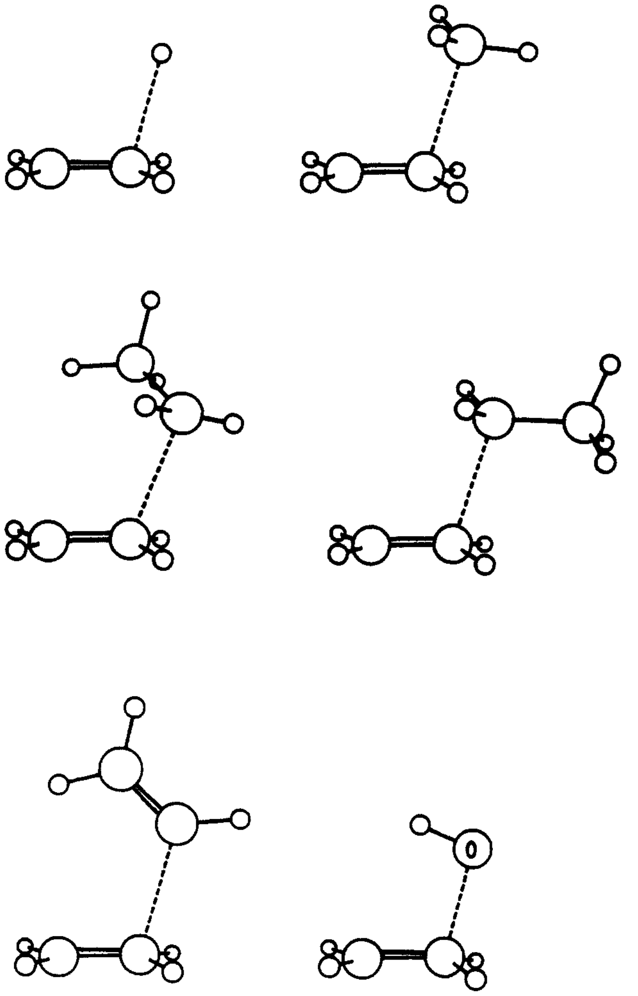

Figure 1. 3-21G transition structures for radical additions to ethylene. Radicals are H•, Me•, Et• (adding gauche and anti), $CH_2{=}CH$•, and HO•. Table I gives more geometrical details.

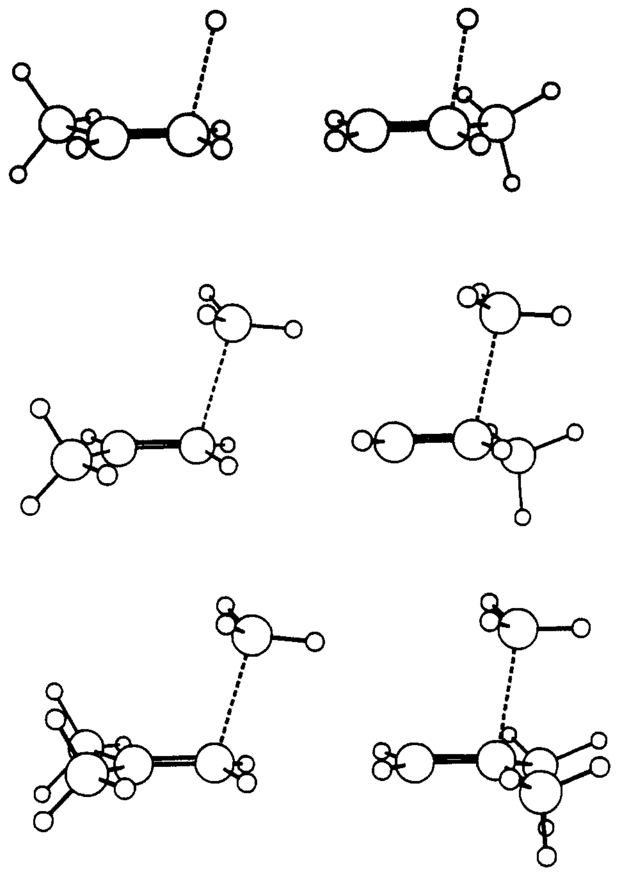

Figure 2. 3-21G transition structures for H• and CH_3• additions to C_1 and C_2 of propene and CH_3• additions to C_1 and C_2 of 2-methylpropene. Table II gives more geometrical details.

determined experimentally.[24] However, this agreement may be fortuitous, since both theoretical and experimental data are subject to considerable error. The theoretical activation energies listed are for hypothetical vibrationless species, and were not corrected by zero-point energies, which differ somewhat for reactants and transition structures.[11] Furthermore, the basis sets used in our work (3-21G or 4-31G in one case) are relatively small, and some error is expected for this reason. The activation energies are calculated from RHF results for alkenes and UHF for radicals and transition structures. The UHF wave functions are not pure doublet states, since spin contamination by states of higher multiplicity is found.[25] The values of S^2 are 0.96–1.05 for the transition structures studied, whereas $S^2 = S(S + 1) = 0.5(1.5) = 0.75$ for a pure doublet state. The stabilizing admixture of states of higher multiplicity which occurs in UHF, but not in reality, may compensate fortuitously for the neglect of correlation energy, which sould stabilize the transition structures more than the reactants. Schlegel and Sosa have determined the effect of basis set and correlation energy upon transition structures and energy for the addition of HO• to ethylene. At the 3-21G level, the activation barrier is 5.3 kcal/mol. The barrier is 8.7 kcal/mol by using the 6-31G* basis, drops to 3.3 kcal/mol with correlation energy corrections (MP4SDQ), and drops further to 1.8 kcal/mol when zero-point energy corrections are made.[10] A comparison of the 3-21G and 6-31G* transition structures for HO• addition to ethylene (Table I) indicates that geometries are not changed much by alteration of basis set. The 3-21G and 6-31G* two geometries are the same to within a few hundredths of an Angstrom for bond lengths and a few degrees for all angles.

Recent experimental measurements of the rate of addition of hydroxyl radical to ethylene indicate that this reaction has no barrier and, indeed, a negative activation energy.[24b] Thus, our prediction of a 5.3 kcal/mol activation energy for this process is in considerable disagreement with experiment.

Schlegel has located the transition structures for the addition of H• to ethylene and fluoroethylene and of F• to ethylene at the 3-21G, 6-31G*, and MP2/3-21G levels.[11,12] For the addition of H• to ethylene, the forming HC and breaking CC double bond lengths are respectively 2.017 and 1.354 Å by 3-21G, 2.004 and 1.358 Å by 6-31G*, and 1.845 and 1.346 Å by MP2/3-21G calculations. Bond angles are within 2° of each other in each of these calculations. Bond lengths and angles are not particularly sensitive to the basis set. However, inclusion of correlation energy corrections at the MP2/3-21G level causes the transition structure to become appreciably later in terms of the forming CH bond length but extremely early according to the CC bond length, which is only 0.005 Å longer than that calculated for ethylene at the same level.

The transition structure for the reaction of methyl radical with ethylene is similar to that found by Dewar and Olivella with MINDO/3 at the UHF level (UMINDO/3) or with the half-electron method.[13] The UMINDO/3 transition structure is earlier than our ab initio 3-21G structure, with the forming bond length equal to 2.36 Å

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(25) Szabo, A.; Ostlund, N. S. *Modern Quantum Chemistry*; MacMillan: New York, 1982; pp 104 ff, 205 ff.

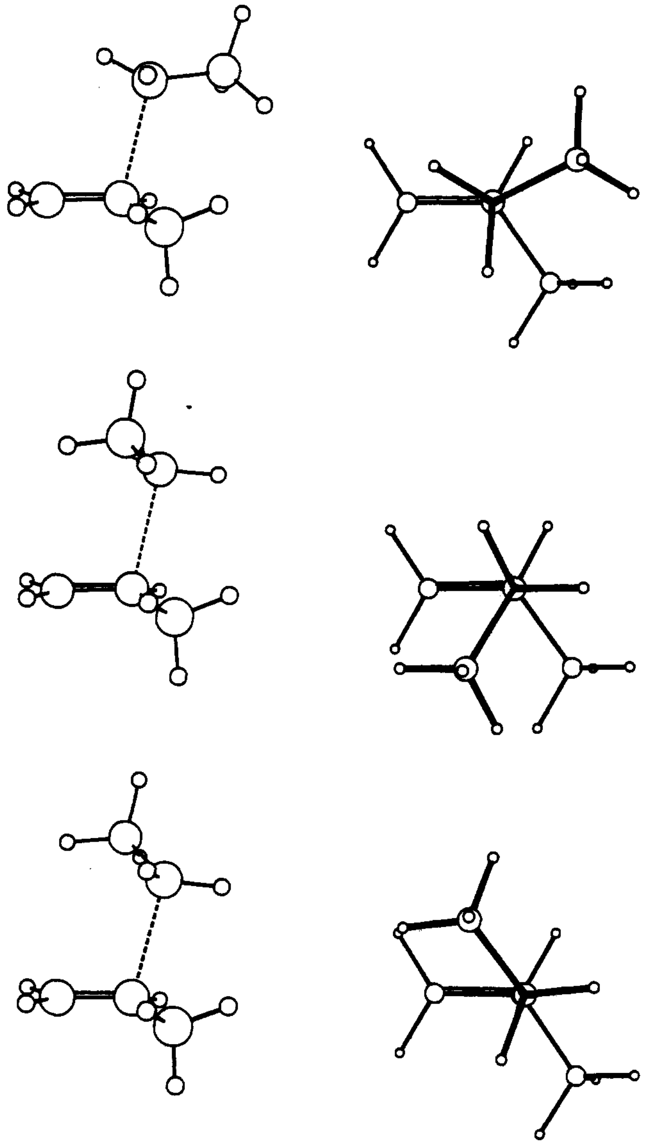

Figure 3. 3-21G transition structures for addition of $CH_3CH_2^\bullet$ to C_2 of propene. Table III gives more geometrical details.

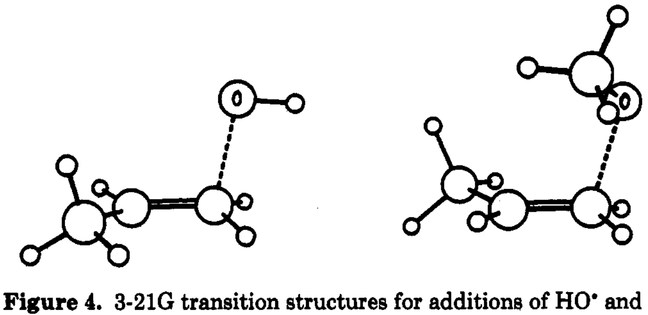

Figure 4. 3-21G transition structures for additions of $HO^\bullet$ and $CH_3O^\bullet$ to propene. Table IV gives more geometrical details.

and showing correspondingly less pyramidalization about the ethylene moiety. The angle of attack is essentially identical with that found here, as is the staggered arrangement about the forming CC bond. Although the angles are not given in the paper, there is apparently no pyramidalization of C_2 or the ethylene in the UMINDO/3 transition structure.[13]

These comparisons establish the relative insensitivity of radical addition transition structures to computational methods. It is clear from the variations in transition structure and activation energies reported by Schlegel that very high level calculations will be necessary to achieve accurate activation energies, but the qualitative features of transition structures and relative activation energies for regioisomeric transition structures (see ref 7 and results below) are obtained even at the UHF/3-21G level used in this work.

Attack Angles and Reactant Distortions. A point of major interest in our calculations is the angle of attack of the radical on the alkene and how this attack angle varies with the nature of the radical and the alkene substituent. The attack angle is remarkably constant, varying only from 102 to 109° for attack of a variety of radicals on ethylene or on C_1 or C_2 of propene or isobutene. Thus, radical additions on a methylene terminus occur at an approximately tetrahedral angle, but the angle is decreased by substitution, presumably due to steric effects. For the methyl or ethyl radical additions reported in Table I–III, attack on a $=CH_2$ terminus occurs with a transition structure attack angle (θ_1) of 108–109°, attack on a $=CHCH_3$ occurs with an attack angle of 104–105°, and attack on a $=C(CH_3)_2$ terminus occurs with an attack angle of 102°. Lefour et al. found that the normal 105–107° angle of attack of $H^\bullet$ on a CH_2 terminus is decreased to 97° for attack on the $=CHNH_2$ terminus of vinylamine.[7] Thus, as the repulsion between the radical and the substituents at the alkene terminus increases, the attack angle decreases. When there is attraction between the radical and the substituent, the angle of attack increases. For example, in the attack of $H^\bullet$ on C_1 of vinylborane,[7] θ_1 increases to 110°.

There is a barely preceptible alteration in attack angle with variation in the nucleophilic or electrophilic character of the radical. Thus, proceeding from nucleophilic to electrophilic radicals in the series, $CH_3CH_2^\bullet$, $CH_3^\bullet$, $CH_2{=}CH^\bullet$, $H^\bullet$, $CH_3O^\bullet$, and $HO^\bullet$, the angles of attack on $=CH_2$ termini are 109°, 108°, 107°, 106°, 108°, and 103–106°, respectively. While this trend is in accord with expectation that nucleophilic species attack with larger angles than electrophilic,[2b] the variations are barely significant.

Kwart proposed that electrophilic alkoxy radicals, such as *tert*-butoxy, attack alkenes at an acute angle.[26] However, a decrease in attack angle of of only a few degrees is found in the calculations on $HO^\bullet$ or $CH_3O^\bullet$, as compared to that found in $H^\bullet$ or $R^\bullet$ transition structures.

For hydrogen atom addition to ethylene, we evaluated qualitatively the ease of deformation of the attack angle away from equilibrium by varying this angle by 5° in the plane of symmetry and out of the plane of symmetry.[2b] We found that distortion of the attack angle for radical addition requires only 25% of the energy required to perform a similar distortion in the product, and in-plane bending is somewhat easier than out-of-plane bending. Thus, although the transition states are relatively early, the angle of attack is relatively tightly proscribed.[27]

In the addition of $H^\bullet$, $CH_3^\bullet$, and $HO^\bullet$ to ethylene, the partially formed CH, CC, and CO bond lengths are 85%, 46%, and 33% longer than these bonds in the fully formed products. The extent of bond formation indicates that hydrogen atom addition occurs earlier than either $R^\bullet$ and $RO^\bullet$ addition. The extent of bond formation, which increases along the series CH < CC < CO, parallels the increasing order of calculated activation energies. That is, the earler the TS, the lower the activation energy. The extent of alkene distortion is also consistent with this

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[26] Kwart, H.; Benko, D. A.; Bromberg, M. E. *J. Am. Chem. Soc.* **1978**, *100*, 7093.

[27] For a review of attack angles in transition states, see: Menger, F. *Tetrahedron* **1983**, *39*, 1013.

observation. For example, the length of the breaking alkene CC double bond and the extent of pyramidalization of both alkene carbons increase along the series $H^{\bullet} < CH_3^{\bullet} < HO^{\bullet}$.

As has been noted previously,[7] although the transition structures are relatively early in terms of bonding changes, the alkene angular distortions are relatively large in the transition structures. The CH_2 flap angle, θ_2, will become approximately 125° in the reaction product, so for $H^{\bullet}$, $R^{\bullet}$, and $HO^{\bullet}$ additions, this angle change has progressed 20%, 33%, and 45% toward the product value, respectively. There is slightly greater pyramidalization of the alkene terminus under attack when this terminus is substitution (Table II).

In each reaction, there is a small but significant tendency toward trans bending of the alkene. Similar trends have been noted earlier for radical additions to alkenes,[7,8] and a much larger trans bending tendency is found for nucleophilic additions.[28] The value of θ_2 ranges from 2 to 6° in the various transition structures and is similar to the degree of pyramidalization calculated for substituted alkyl radicals.[29] As found for the latter, the pyramidalization of C_2 occurs in such a direction to produce staggering about the C–C bond. Such a distortion also best maintains overlap between the distorted p orbitals at C_1 and C_2.

Conformations in Transition Structures. In our earlier papers, we have reported the conformational preferences of allylic groups in the transition structures of electrophilic, radical, and nucleophilic additions to multiple bonds.[2] For $H^{\bullet}$, $HO^{\bullet}$, and $CH_3O^{\bullet}$ additions to C_1 of propene, the allylic bonds are rotated away from those present in the equilibrium conformation of reactants. The preferred conformation of the methyl group in propene has one CH bond of the methyl eclipsed with C═C. The resulting HCC═C dihedral angles are 0°, 120.5°, and −120.5° at the 3-21G level. For the very early $H^{\bullet}$ + propene (C_1) transition structure, these angles are slightly altered to 5°, 125°, and −116°. This corresponds to a rotation toward a staggered geometry with respect to the slightly pyramidal C_2. As pyramidalization increases for $CH_3^{\bullet}$, $HO^{\bullet}$, and $CH_3O^{\bullet}$ attack on C_1 of propene, the staggering increases. For $CH_3^{\bullet}$ attack on C_1, the methyl attached to C_2 has HCC═C dihedral angles of 9°, 129°, and 111°. For $HO^{\bullet}$ attack at C_1, the C_2 methyl dihedral angles are 26°, 147°, −94°. For $CH_3O^{\bullet}$ attack, these angles are 16°, 137°, and −104°. For comparison, these dihedral angles will be approximately 60°, 180°, and −60° in the reaction products.

For radical additions to C_2 of propene, the allylic groups are staggered with respect to the forming bonds and to the other two bonds to the partially pyramidal C_2.[2b] For example, the allylic torsion angles of the methyl hydrogens are 28°, 149°, and −92° for $H^{\bullet}$ attack on C_2 of propene. We showed earlier that the methyl rotational barrier in this transition structure is approximately 2 kcal/mol.[2b] As can be seen in Figure 2, the methyl groups of propene and 2-methylpropene are also staggered with respect to C_2 upon attack of $CH_3^{\bullet}$ on C_2 of these alkenes. The torsion angles are 39°, 160, and −81° in these transition structures.

There is a tendency for staggering with respect to the forming bond in additions of alkyl radicals. For the addition of the methyl radical to ethylene, the barrier to rotation about the forming CC bond is 0.6 kcal/mol, which is only 20% of the barrier to rotation in propane. The eclipsed conformer is not a true transition structure, since the force constants for motions both along the reaction coordinate (C–C bond formation) and for methyl rotation about the forming CC bond are negative. The stationary point corresponding to the eclipsed attack of $CH_3^{\bullet}$ on ethylene has two imaginary frequencies, one with a frequency of $439i$ cm^{-1} for motion along the reaction coordinate (cf. $421i$ cm^{-1} for staggered attack) and the second equal to $101i$ cm^{-1} for methyl rotation.

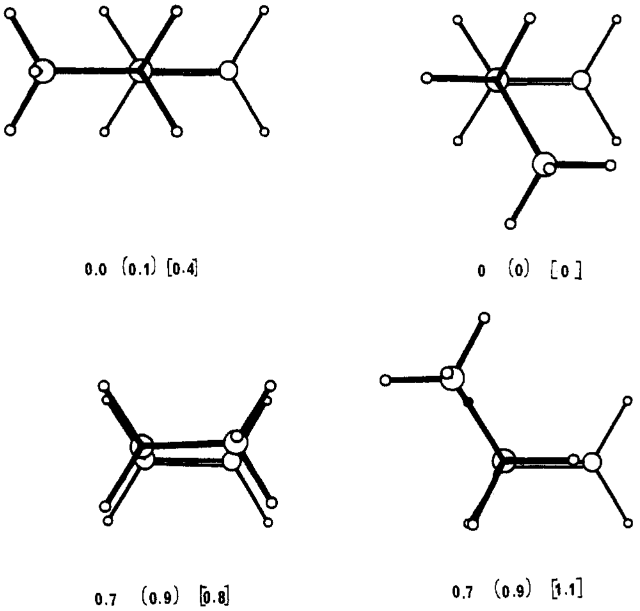

Figure 5. Newman projections of 3-21G transition strucutres for addition of $CH_3CH_2^{\bullet}$ to ethylene. The structures with CCC═C constrained to 0° and 120° are also shown. 6-31G*//3-21G relative energies are given in parentheses, and MP2/6-31G*//3-21G relative energies are given in brackets.

All of the additions of alkyl radicals show a similar staggered arrangement with respect to the forming bonds. As summarized in Figure 5, the energies of various conformations were calculated here at various levels, although geometries were optimized only with the 3-21G basis set. All methods place the staggered transition structure lower in energy than eclipsed. For ethyl radical addition to ethylene, the gauche (∠C——C—C═C = 60°) transition structure is only 0.4 kcal/mol lower in energy than the corresponding anti (∠C——C—C═C = 180°) transition structure at the highest computational level used. Thus, the steric repulsion between CH_3 and CH_4 is lower than that between CH_3 and H, due to the relatively large C——C length in the transition structure. Two eclipsed transition structure models were calculated with C—C—C═C constrained to 0° and 120° (Figure 5). These are energy maxima with respect both to addition and to torsion about the forming CC bond and are not authentic transition structures. These are 0.7–1.1 kcal/mol higher in energy than the staggered transition structures. In the ∠C—C—C═C = 0° case, the angle θ_1 is somewhat larger than in most additions (109.2° vs. 107.8°). This is a result of repulsion between the terminal CH_2 group of the alkene and the methyl group. Nevertheless, there is a tendency for the group to be eclipsed with the π bond in preference to 120°, a preference which has been proposed in order to rationalize the preferred cis stereoselectivity of the cyclization of the 1-methyl-5-hexenyl radical.[5a] By contrast to the ethyl radical results, attack of the vinyl radical on ethylene occurs preferentially, so that the vinyl group is eclipsed with the double bond of ethylene (CCCC = 0°), as shown in Figure 1. The structures with CCCC = 120° and 180° are 0.6 and 0.3 kcal/mol higher in energy.

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Three transition structures were located for the addition of the ethyl radical to C_1 of propene. These are depicted in Figure 3, and Newman projections are given also. The anti arrangement, A, of the methyl groups is favored. The two gauche arrangements, B and C, are 0.4 and 0.5 kcal/mol higher in energy than the anti. These results indicate that gauche methyl–methyl repulsion of methyls attached to a forming C–C bond is about half that of a gauche methyl–methyl repulsion in butane. Once again, the methyl–methylene repulsion is insignificant, and only the methyl–methyl interactions determine the relative energies of the different transition structures.

This result is marginally relevant to the topological rule proposed by Seebach and Golinski to account for the erythro–threo (syn–anti) type stereoselectivities observed in aldol and related reactions involving electrophilic and nucleophilic unsaturated systems.[30] In particular, for the radical additions, there is always a preference for staggering, as in the Seebach–Golinski topology. However, whereas there appear to be special effects that fix the remaining conformational preferences about the forming CC bond in aldol and related reactions,[30] for radical additions, there are only normal steric effects which favor anti–alkyl groups. In the attack of methyl radical on ethylene, the angles with respect to the forming bond are 100.1° for the anti hydrogen on the methyl, and 101.0° for the gauche hydrogens. There is essentially identical pyramidalization of the methyl radical with respect to the forming bond. The angles of the ethylene terminus are 107.8° for the CCC angle and 90.3° for the HCC angles.

The vinyl radical prefers to add with the C=C——C——C dihedral angle = 0°. Conformations with dihedral angles of 180° and 120° have energies that are 0.3 and 0.6 kcal/mol higher. The 120° conformer is not a true transition strucutre but is an energy maximum with respect both to rotation about the forming bond and to CC bond formation. Vibrational frequencies were not calculated for the 180° structure, but it is likely that this is a real transition structure, since the 120° structures are higher in energy. The preference for the eclipsed conformation is presumably related to the preference for an allylic bond in the product to be eclipsed with respect to the double bond. The preferred conformation of 1-butene has an allylic CH bond eclipsed with the double bond, and the conformation with the CC bond eclipsed with the double bond is ~0.5 kcal/mol higher in energy. The preferred transition structure has the methylene and methyl groups very far apart even though they are eclipsed, so that steric effects do not disfavor this transition structure. It is surprising that the 180° rather than the 120° conformation is a second transition structure.

$HO^\bullet$ and $CH_3O^\bullet$ additions favor that staggered arrangement which places the HO or CO bonds of the substituent gauche with respect to the C=C of the alkene. The stationary point with the anti arrangement of the $HO^\bullet$ bond is 0.8 kcal/mol higher in energy for addition of $HO^\bullet$ to ethylene. When the CO bond is anti in the $CH_3O^\bullet$ plus propene transition structure, the energy is 0.2 kcal/mol higher in energy. The gauche arrangement is presumably preferred in order to minimize repulsion between the oxygen lone pair electrons and the alkene π electrons.

Regioselectivity. Although orientation phenomena are often described in terms of electronic effects with the more stable radical being favored kinetically, many authors have pointed out that steric effects better account for the general preference for radicals to add to the less substituted terminus of an unsymmetrical alkene.[6,7813] The calculations reported in Table II are in full accord with the steric explanation for regioselectivity in addition to the nonpolar alkenes. Attack of $H^\bullet$ on C_1 of propene is calculated to have a slightly (0.2 kcal/mol) higher activation energy than attack on ethylene. Experimental data are not sufficiently precise to determine if this energy difference is correct.[24] The calculations indicate that there is no electronic effect by the remote methyl. Attack at C_2 on propene has a 1.6 kcal/mol higher activation energy than attack at C_1. Attack of methyl radical on C_1 of propene has an 0.5 kcal/mol higher activation energy than attack of $H^\bullet$ on ethylene. As is found for $H^\bullet$ attack, there is no indication of stabilization of the transition structure by the methyl group at C_2 of propene. The difference between activation energies for ethyl radical attack at C_1 and C_2 is 1.9 kcal/mol, somewhat higher than calculated for $H^\bullet$ attack. For addition of $CH_3^\bullet$ to 2-methylpropene, attack at C_1 is 3.8 kcal/mol more favorable than attack at C_2.

Dewar and Olivella studied the additions of methyl radical to both termini of propene.[13] They found that the activation energy for attack at C_1 of propene occured with an activation energy that is 4.3 kcal/mol lower than attack at C_2. All of these results indicate that steric rather than electronic effects determine the orientation of attack.

Nevertheless, there are special cases in which electronic rather than steric effects influence regioselectivity. Thus, methyl radical adds to the disubstituted terminus of trifluoroethylene, and this has been attributed to the result of electronic and thermodynamic factors.[31] In spite of isolated cases of this type, in alkylethylenes (such as studied here) steric effects appear to control regioselectivity.

Conclusion

The transition structures for radical additions to alkenes provide useful insights into the details of geometry and energetics of these processes. These results have also been used for the development of a quantitative model for interpretation of regioselectivity and stereoselectivity in intramolecular radical addition reactions.[4]

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Registry No. H, 12385-13-6; $CH_3^\cdot$, 2229-07-4; $CH_3CH_2^\cdot$, 2025-56-1; $H_2C{=}CH^\cdot$, 2669-89-8; $HO^\cdot$, 3352-57-6; $CH_3O^\cdot$, 2143-68-2; ethylene, 74-85-1; propene, 115-07-1; 2-methyl-2-butene, 513-35-9.

Supplementary Material Available: Optimized internal coordinates and energies for calculated transition strucutre (18 pages). Ordering information is given on any current masthead page.

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