tainties, the latter value is consistent with the D_0 value of 39.3 ± 2.0 kcal/mol for Fe^+–CO. The agreement found in the D_0 values for Fe^+–CO shows that the AE for reaction 5 determined in the PEPICO measurement is reliable.

IV. Conclusion

We have carried out a detailed study of processes 1–6 by using the PEPICO method. The bond dissociation energies for CO–$Fe(CO)_n^+$, n = 0–4, at 0 K are calculated by using the IE for $Fe(CO)_5$ and the AEs for the formation of $Fe(CO)_n^+$, n = 0–4. The D_0 value for Fe^+–CO thus determined by the PEPICO measurement is in accord with that obtained in the collision-induced dissociation study and the prediction of the recent ab initio calculation.

As the internal energy for $Fe(CO)_5^+$ is increased from 0 to 6.51 eV, the dissociation of $Fe(CO)_5^+$ may take place by sequential loss of CO. In the internal energy range of 6.51–8.65 eV, the PEPICO intensities for $Fe(CO)_2^+$, $FeCO^+$, and Fe^+ are finite, indicating that $Fe(CO)_2^+$ may dissociate directly to both $FeCO^+$ and Fe^+.

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Transition Structures for Hydrogen Atom Transfers to Oxygen. Comparisons of Intermolecular and Intramolecular Processes and Open- and Closed-Shell Systems

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Abstract: The transition structures for the intramolecular hydrogen atom abstractions of the butoxy radical, the triplet and the radical cation states of butanal, and the radical cation of butanol, as well as that of the thermal retro-ene reaction of butanal, were located with ab initio molecular orbital calculations. These processes are the rate- and/or product-determining steps in common reactions like the Barton reaction, the Norrish type II photochemical reaction, and the McLafferty rearrangement of radical cations in mass spectrometry. The corresponding intermolecular hydrogen abstractions from methane by the methoxy radical, triplet formaldehyde, formaldehyde radical cation, and the methanol radical cation were located for comparison, using UHF theory and correlation theory corrections at the MP2 level. Differences in activation energy are related to the electronic differences between closed-shell, open-shell, and charged open-shell systems. Regioselective hydrogen atom transfer in the Norrish type II reaction is due to a combined enthalpic and entropic preference for a six-membered-ring transition structure. Our calculations indicate a strong preference for in-plane hydrogen abstraction by triplet aldehydes.

Introduction

Hydrogen atom transfers are ubiquitous reactions in organic chemistry. These reactions have many features in common with proton transfers, events that are of fundamental importance in most branches of chemistry. There have been a number of quantitative theoretical treatments of hydrogen atom transfers, starting with early investigations of the reaction between a hydrogen atom and a hydrogen molecule.[1] In recent times, theoretical treatments have been applied to more complex systems.[2] The most commonly studied type of hydrogen atom transfer involves the abstraction of an alkyl hydrogen by an oxygen species having an unpaired electron.[3] *Intramolecular* hydrogen atom abstractions by various reactive oxygen functionalities generally involve six-membered-ring transition states and are often accompanied or followed by skeletal rearrangements or fragmentation. Until recently, high-level quantum chemical calculations on the systems in question were not practical. Recently, several semiempirical calculations have been reported for the McLafferty rearrangement and the Norrish type II reaction,[4-6] and one ab initio calculation has been reported on the McLafferty rearrangement.[7]

We have undertaken ab initio molecular orbital computational studies of the most important processes (see Scheme I) of this kind in solution and in the gas phase: (1) the Barton reaction,[8] (2) the Norrish type II cleavage,[9] (3) the McLafferty rearrangement,[10] and (4) the related reactions of alcohol and ether radical cations.[10,11] The analogous reaction of a closed-shell species is the retro-ene reaction of carbonyl compounds (5).[12] This paper describes the results of our calculations on these processes and on the related intermolecular reactions. We are in the process of developing force fields for these processes similar to that we have reported for reaction 1.[13,14] Our calculations were designed

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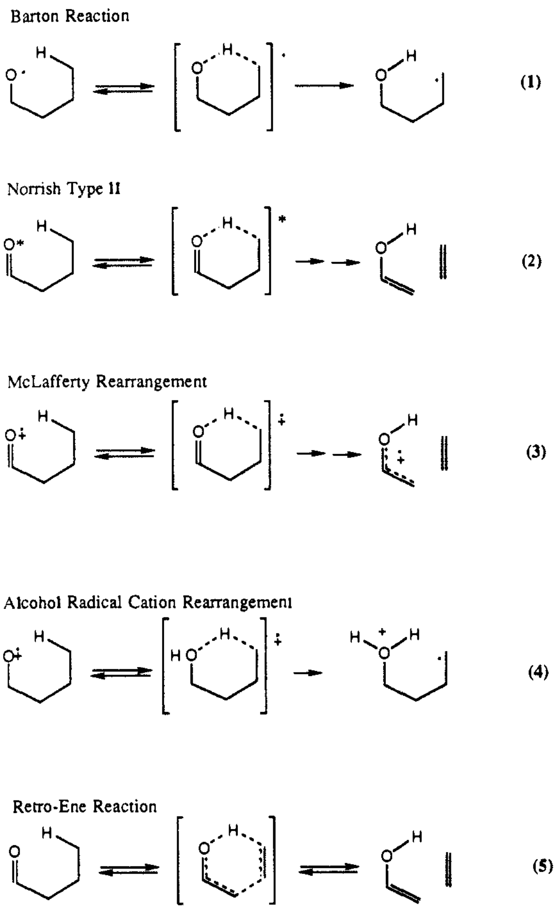
Scheme I



to elucidate a variety of interesting features of these reactions, as enumerated below.

(1) What is the preferred geometry of hydrogen atom transfer in these reactions, and how rigid are the transition states? The points of particular interest are the angle about the transferring hydrogen, the distances between the heavy atoms involved in the hydrogen transfer, and the angles between bonds and partial bonds at these heavy atoms. It is generally believed that linear hydrogen transfer should be preferred but that bending away from linearity should be relatively easy.[13-15] It has been proposed that there is a direct relationship between the O•, H–C distance in reactants and the rate of Barton reactions,[8d] but we have focused attention on the heavy atom distance accessible in the transition state. Brun and Waegall proposed that the rate of hydrogen abstraction would be very low for reactants with an O···H distance greater than 2.1 Å.[8d] For the McLafferty rearrangement, Djerassi has proposed that no intramolecular hydrogen abstraction occurs if the oxygen–hydrogen distance is greater than 1.8 Å. For the Norrish type II reaction, an additional point of interest is the geometry at the excited carbonyl oxygen, since it has been proposed that hydrogen abstraction should occur in the plane.[15,16]

(2) Are these reactions, which involve both hydrogen transfer and C–C bond cleavage, stepwise or concerted? While the Barton reaction results only in hydrogen transfer followed by trapping of the resulting carbon radical, the McLafferty rearrangement and Norrish type II reactions involve CC cleavage, either subsequent to or simultaneously with, hydrogen abstraction. There is experimental evidence for a stepwise mechanism for both the Norrish type II and the McLafferty reactions.[16,17]

(3) The retro-ene reaction, like many other orbital-symmetry-allowed pericyclic processes, is likely to be concerted.[12b] Reactions 1–4 are similar in that they generally exhibit a preference for a six-membered cyclic transition state,[18a-c] although a seven-membered transition state can compete in the Norrish type II cleavage if the connecting chain contains double bonds.[18b] We have recently predicted that, for alkoxy radicals, this preference is dictated by a favorable entropy at room temperature, since enthalpically the seven-membered transition state is favored by 0.8 kcal/mol.[14] Are the six-membered preferences observed for all of these reactions a consequence of entropic preferences, or are energetic factors important in some cases?

(4) How are the activation energies of these processes influenced by the nature of the oxygen species? Do all of these processes have barriers?

In order to answer as many of these questions as we could, and to develop general information about the geometries and force constants of such transition structures for future development of empirical force fields for these processes, we have carried out calculations on transition structures of intramolecular hydrogen abstraction in the butoxy radical (**1**),[14] the triplet (**2**) and radical cation (**3**) states of butanal, the radical cation of butanol (**4**), and the thermal retro-ene reaction of butanal (**5**). We have also calculated the transition structures of the simple intermolecular processes for comparison and to determine the influence of correlation energies on geometries.

Calculations

Optimized geometries of the reactants and transition structures for the intramolecular reactions were located with GAUSSIAN 82[19] or GAUSSIAN 86,[20] using the 3-21G basis set[21] and Hartree–Fock theory. Unrestricted Hartree–Fock theory, which allows different orbitals for each electron, was employed for all open-shell species. Vibrational frequencies were calculated by a normal coordinate analysis on force constants determined analytically for all stationary points which were located. For transition structures, the second derivative matrix was found to have only one negative eigenvalue corresponding to hydrogen atom transfer. Since correlation energies influence activation energies signficantly, single-point energy calculations were performed at the MP2/6-31G* level[21,22] on the HF/3-21G optimized geometries of the intramolecular transition structures. A summary of the calculated SCF and MP2 energies and activation parameters is given in Table I. For each of the starting materials, more than one conformation was investigated, but only the lowest energy conformation for each species is reported in Table I. The transition structures for these reactions are shown in Figure 1. The data for the corresponding intermolecular reactions are given in Table II and Figure 2. Since these systems are much smaller, geometries were optimized at the UHF/6-31G* and UMP2/6-31G* levels. In Table II, spin-projected PMP2/6-31G* energies are given to correct for spin

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Table I. Energies of Reactants, Transition Structures, Products, and Activation Parameters for Intramolecular Reactions[a]

	total energy, au		E_{rel}, kcal/mol				
molecule	UHF/31-21G	MP2/6-31G*	UHF/3-21G	UMP2/6-31G*	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta G^{\ddagger}$(25 °C)
butoxy radical (1)							
reactant[b]	−230.25690	−232.18555	0.0	0.0			
TS	−230.20173	−232.16181	34.6	14.9	11.0	−3.6	12.1
product	−230.23094	−232.18602	16.3	−0.3			
triplet butanal (2)							
reactant[c]	−229.63103	−231.53847	0.0	0.0			
TS	−229.57920	−231.51617	32.5	14.0	9.7	−4.8	11.1
product	−229.60580	−231.53516	15.8	0.7			
butanal radical cation (3)							
reactant[d]	−229.38547	−231.30938 −231.33763[e]	0.0	0.0 0.0[e]			
TS	−229.36073	−231.31506 −231.33511[e]	15.5	−3.6 1.6[e]	−6.8	−10.1	−3.8
product	−229.37938	−231.31809	3.6	−5.5			
butanol radical cation (4)							
reactant[f]	−230.54554	−232.45813	0.0	0.0			
TS	−230.53121	−232.47569	9.0	−11.0	−13.1	−7.1	−11.0
product	−230.56719	−232.49217	−13.6	−20.8			
butanal (5)							
reactant	−229.69704	−231.67804	0.0	0.0			
TS	−229.58008	−231.56904	73.4	68.4	64.2	−4.9	65.7
products	−229.64275	−231.60238	34.1	47.5			

[a] Activation energies were calculated from the UMP2 energies by correcting for zero-point energies and for the RT and C_pT terms (T = 298 K) obtained with the 3-21G basis set. Entropies were derived from the calculated geometries and harmonic vibrational frequencies. Correction factors of $T \ln 9$ are added to the reactants to account for the number of available conformations and of $R \ln 2$ to the transition states to allow for the existence of an enantiomeric TS in each case. A correction factor of 4.4 eu[13,31] is added to the transition states **1**, **2**, and **4** to account for their low-frequency puckering vibration (pseudorotation). [b] This conformation has a gauche arrangement of the OCCC atoms and an anti arrangement of the CCCC atoms; another reactant conformer having an anti arrangement of the OCCC atoms and of the CCCC atoms is 0.4 kcal/mol higher in energy at the MP2/6-31G* level.[13] [c] This conformation has an anti arrangement of the OCCC atoms and an anti arrangement of the CCCC atoms; two other reactant conformers each having a gauche arrangement of the OCCC atoms and an anti and gauche arrangement of the CCCC atoms, respectively, are very close (0.1 and 0.2 kcal/mol) in energy to the most stable conformer at the HF/3-21G level. [d] This conformation has a syn arrangement of the OCCC atoms and an anti arrangement of the CCCC atoms; another reactant conformer having a syn arrangement of the OCCC atoms and a gauche arrangement of the CCCC atoms is very close (<0.1 kcal/mol) in energy to the most stable conformer, at both HF/3-21G and MP2/6-31G* levels. [e] These are PMP2 energies of fully optimized MP2/6-31G* structures; all other other entries in these columns are MP2/6-31G*//3-21G energies. The lowest energy conformation of the reactant was assumed to be the anti conformer, as above; the gauche conformer was not optimized at this level. [f] This conformation has a gauche arrangement of the OCCC atoms and an anti arrangement of the CCCC atoms; another reactant conformer having an anti arrangement of the OCCC atoms and of the CCCC atoms is very close (<0.1 kcal/mol) in energy to the most stable conformer at the HF/3-21G level.

Table II. Energies of the Reactants, Transition Structures, and Products for Reactions 6–9

	total energy, au		E_{rel}, kcal/mol	
	UHF/6-31G*	PMP2/6-31G*[a]	UHF/6-31G*	PMP2/6-31*[a]
methoxy radical (6)				
$CH_3O^{\cdot} + CH_4$	−154.61592	−155.03204	0.0	0.0
TS	−154.55616	−155.00622	39.8	16.2
$CH_3OH + CH_3^{\cdot}$	−154.59441	−155.02834	15.8	2.3
triplet formaldehyde (7)				
$^3CH_2O + CH_4$	−153.98978	−154.38545	0.0	0.0
TS	−153.93011	−154.35756	37.4	17.5
$^{\cdot}CH_2OH + CH^{3\cdot}$	−153.96775	−154.38014	13.8	3.3
formaldehyde radical cation (8)				
$CH_2O^{\cdot+} + CH_4$	−153.71661	−154.11821	0.0	0.0
reactant complex		154.12455		−4.0
TS	−153.69726	−154.11927	12.1	−0.7
product complex		154.14887		−19.2
$^+CH_2OH + CH_3^{\cdot}$	−153.71542	−154.12684	0.7	−5.4
methanol radical cation (9)				
$CH_3OH^{\cdot+} + CH_4$	−154.88239	−155.30146	0.0	0.0
reactant complex		155.31289		−7.2
TS	−154.86981	−155.30493	7.9	−2.2
product complex		155.34763		−29.0
$CH_3OH_2^+ + CH_3^{\cdot}$	−154.89798	−155.32800	−9.8	−16.7

[a] Spin-projected energies are reported for the UMP2/6-31G* geometries.

contamination, which occurs in the UMP2/6-31G* wave functions.

Results and Discussion

Energetics of Intramolecular Processes. The activation energies and reaction energies are much too high at the RHF 3-21G level. While the heats of reaction are reasonable at the MP2/6-31G*//3-21G level, the activation energies for **1** and **2** are still too high.[2,13] The calculated activation energy barrier of 14.9 kcal/mol for the Barton reaction 1 is very close to the value of 14.0 kcal/mol for the Norrish type II reaction, 2. The calculated activation energies are greater than typical experimental values of 5–10 kcal/mol observed for the Barton reaction[18a] and the Norrish type II cleavage.[8a] At the MP2/6-31G*//3-21G level, the McLafferty rearrangement, 3, is predicted to have a negative activation barrier equal to −4 kcal/mol. The McLafferty rearrangement is irreversible under conditions in the mass spectrometer ionization chamber and should have an activation barrier of nearly zero.[10c] Recently, infrared multiple photon (IRMP) experiments

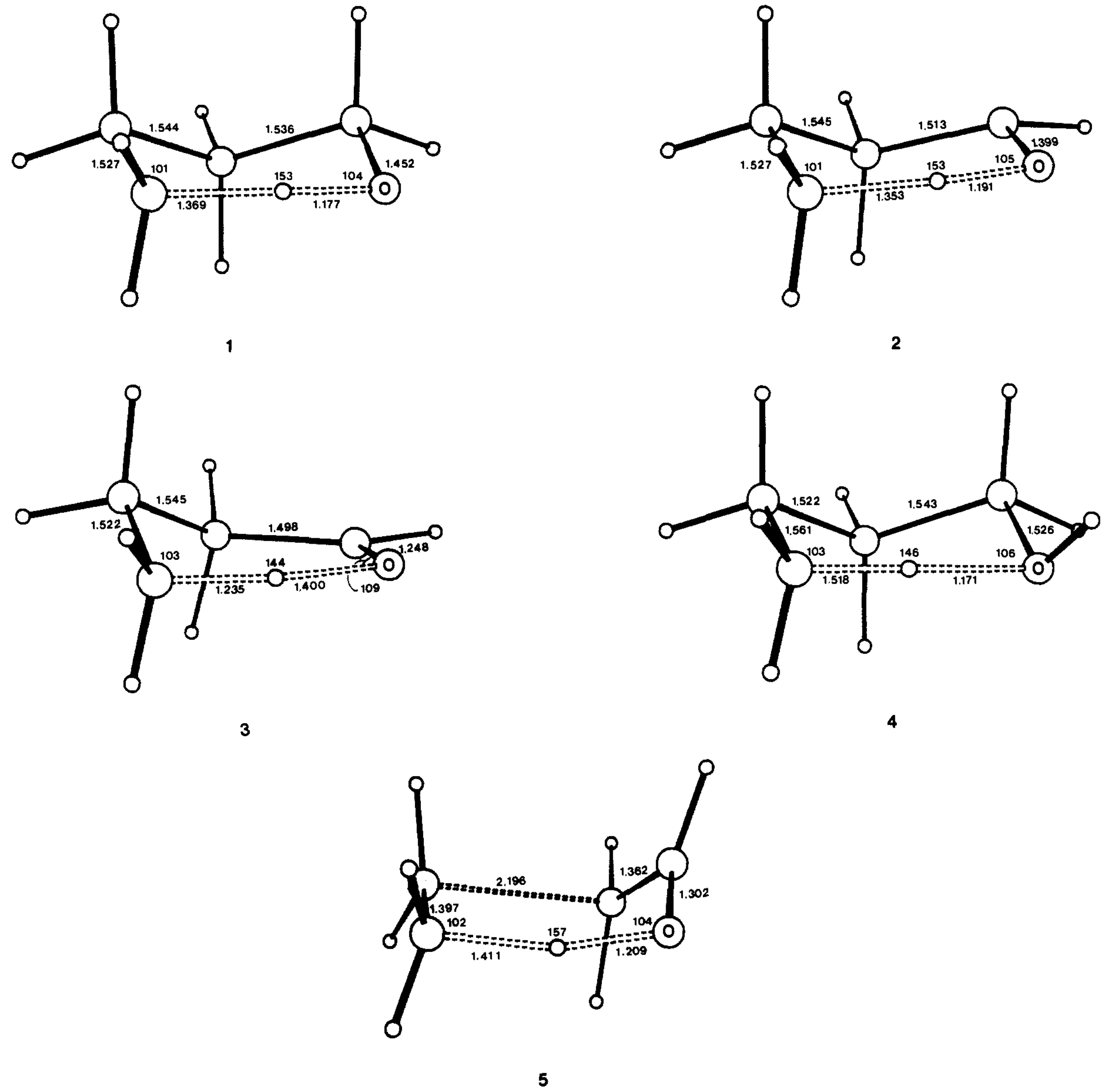

Figure 1. UHF/3-21G transition structures for intramolecular six-membered-ring hydrogen abstractions.

on the activated dissociation of butyrophenone radical cation have indicated a small barrier to reaction.[17b] We have performed MP2/6-31G* optimizations of the reactant and transition structure for **3** and find an activation energy of 1.6 kcal/mol. The rearrangement of ether radical cations, **4**, is predicted to have a large negative activation energy of −11 kcal/mol. The negative activation energy means that the energy maximum in the UHF surface may not exist at the correlated level. It is likely that the barrier is either zero or very small, and the transition structure has a geometry very similar to that of the reactant structures. This reaction is also believed to be irreversible.[11]

In contrast to these low or non-existent barriers, the calculated activation energy barrier of the retro-ene reaction is 68.4 kcal/mol at the MP2/6-31G*//3-21G level. The retro-ene reaction of butanal has never been reported experimentally, and it is expected to have a large activation barrier. The forward ene reaction, for which there are intramolecular examples,[12a] is predicted to have an activation enthalpy of only 17 kcal/mol, lower than related ene reactions of all-carbon systems.[12b]

Energetics of Intermolecular Processes. In reactions 1–5, the calculated activation energies are influenced not only by the affinity of the abstracting oxygen atom for the breaking C–H bond but also by the varying degree of strain in the transition structures, as well as the presence of stabilizing interactions peculiar to some reactants but not others (such as the stabilization of a gauche conformation of the $^{\bullet}OCH_2CH_2CH_2-$ group in the butoxy radical).[14] Such factors are not present in the *inter*molecular processes 6–9, which are related to the Barton, Norrish, and McLafferty reactions, respectively, and the rearrangement of alcohol radical cations. The relative activation energies are thus a better measure of the case of hydrogen atom abstraction by the different types of open-shell oxygen atoms in this series. Geometry optimizations of all reactants, products, and transition states were performed at the UHF/6-31G* and UMP2/6-31G* levels. The relative thermal energies and entropies of reactants, transition states, and products are predictably similar throughout this series, so that the differences in the calculated electronic energies are essentially equal to the calculated differences in free energies.

Qualitatively, the trend in the series 6–9 (Table II) is almost the same as that in the intramolecular reactions 1–4 (Table I). The main difference is that at the MP2/6-31G* level, the activation energies of **6** and **7**, which are very close in all calculations, have reversed order. While HF calculations predict a lower activation energy and reaction energy for **7**, MP2 calculations predict that **6** is lower. MP2/6-31G* single-point calculations on **8** and **9** at the 3-21G geometries gave negative activation energies, just as in the intramolecular reactions. To determine whether a transition structure existed at the correlated level, we performed MP2/6-31G* optimizations on these structures. Authentic transition structures, with one negative eigenvalue corresponding to hydrogen abstraction, were located; however, they were lower in energy than the reactants. This implies that a

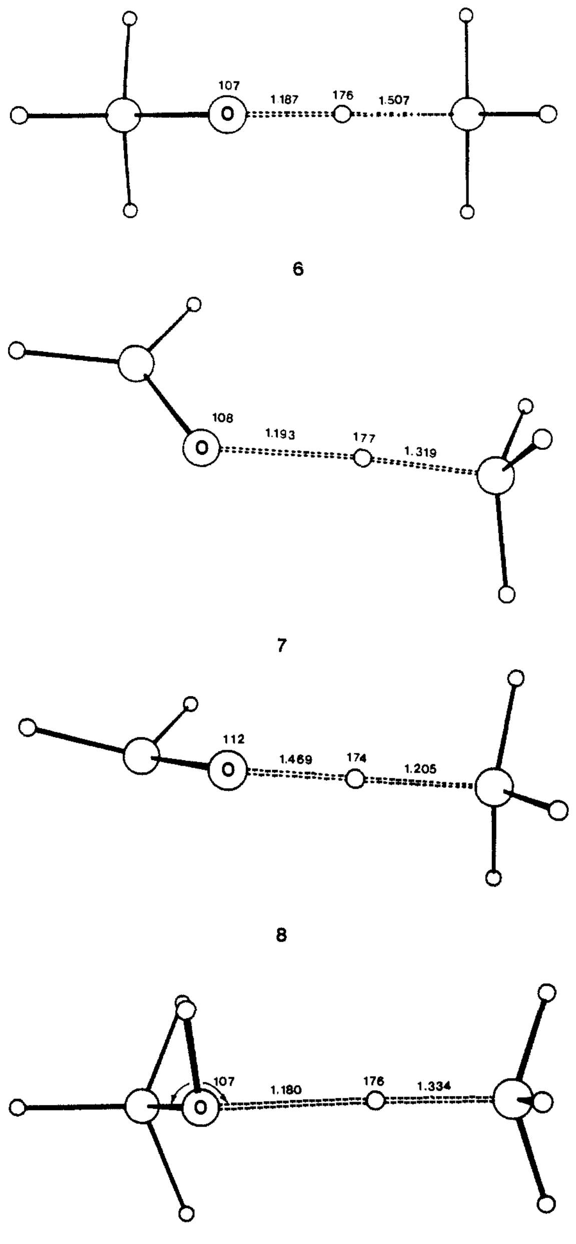

Figure 2. UMP2/6-31G* transition structures for intermolecular hydrogen abstractions.

complex is formed before hydrogen abstraction takes place. Reactant and product complexes were located for **8** and **9**. These complexes are 4 and 7 kcal/mol lower in energy than reactants. From complexes, the hydrogen abstractions have activation energies of 3.3 and 5.0 kcal/mol, respectively, and reaction energies of −15.2 and −21.8 kcal/mol. Comparison of 6-31G* with MP2/6-31G* geometries (Figure 2) shows the earlier nature of the MP2 transition structures, which is also reflected in the activation energies (Table II). The O--H bonds are consistently longer (by 0.05 to 0.43 Å) and the C--H bonds are shorter (by 0.55 to 0.26 Å) in the MP2/6-31G* transition structures. The O--H--C angle is close to 180° in **6** and **7**, as expected for a transferring hydrogen. Surprisingly, this angle becomes much smaller in the MP2 transition structures for **8** and **9**.

When unrestricted HF calculations are performed, contamination of the spin state with contributions from higher multiplicities may present a problem. We examined the extent of this contamination and its effect on energetics by comparing UMP2 with PMP2 energies for reactions 6–9. PMP2 projects out spin contamination from states of higher multiplicity.[20] We found that spin contamination affected mainly the transition structure in reactions 6 and 7. Because of this, spin projection lowered the activation energy by about 2 kcal/mol but did not change the energy of reaction significantly. For reaction 8, contamination was present in the reactants as well as the transition structure. The UMP2 and PMP2 activation energies were about the same, while the reaction energy was increased by about 2 kcal/mol. Spin projection did not affect either the activation energy or the reaction energy of reaction 9, since spin contamination was slight and approximately equal for the reactants, transition structure, and products. These conclusions should also extend to the corresponding intramolecular reactions 1–4.

Table III. Intrinsic Activation Energies for Reactions 1, 2, 5–9[a]

reaction	$\Delta E^{\ddagger}_{i}$	reaction	$\Delta E^{\ddagger}_{i}$
1	15.0	7	15.8
2	13.6	8	9.4
5	41.2	9	13.7
6	15.0		

[a] Calculated from the formula $\Delta E^{\ddagger} = \Delta E^{\ddagger}_{i}(1 + (\Delta E/4)\Delta E^{\ddagger}_{i})^2$.

Intrinsic Activation Energies. The reaction barrier is influenced by the reaction exothermicity, so that the relative activation energies do not represent pure transition state effects. A better measure of such effects is provided by the "intrinsic" activation energy[33] of the reaction, $\Delta E^{\ddagger}_{i}$. According to Marcus' formalism,[23a] $\Delta E^{\ddagger}_{i}$ represents the barrier to reaction when there is no change in free energy from reactants to products ($\Delta E = 0$):

$$\Delta E^{\ddagger} = \Delta E^{\ddagger}_{i}(1 + \Delta E/4\Delta E^{\ddagger}_{i})^2$$

$\Delta E^{\ddagger}_{i}$ therefore represents the contribution of purely transition state effects to the reaction barrier. The intrinsic activation energies, derived from the values of E_{rel} for transition states and products in Tables I and II, are given in Table III. $\Delta E^{\ddagger}_{i}$ was not calculated for reaction 4, because E_{rel} (MP2/6-31G) was found to be negative. ΔE_{i} was calculated for reactions 8 and 9 by using the reactant and product complex energies rather than isolated reactants and products. The retro-ene reaction has a high activation energy that is in the usual range clustered around 35 kcal/mol for pericyclic reactions.[24] This is characteristic of reactions in which a stable closed-shell system must be disrupted in order for the reaction to occur.

Both the radical hydrogen abstraction and the triplet aldehyde reaction have calculated intrinsic barriers around 15 kcal/mol, values that are likely 5–10 kcal/mol higher than actual barriers. This low activation barrier is typical of a radical process, where an open-shell species disrupts a closed-shell species.

Mechanisms. The similarities of the transition structures of reactions 1 and 2, and the almost equal activation energies calculated for the two processes, are in agreement with earlier observations of similarities in the reactions of triplet ketones and alkoxy radicals for both inter-[25] and intramolecular[8] processes. The calculated activation energies are probably 5 kcal/mol higher than experimental values.[8,9] The energies of reaction are also predicted to be almost the same, with the order depending on the level of theory used. The results for the McLafferty rearrangement, 3, are in agreement with numerous experimental findings which suggest that the reaction is stepwise.[10c,18] There is no appreciable stretching of the C–C bond β to the carbonyl group; this bond is actually slightly shorter in the transition structure (1.545 Å) than in the starting material (1.547 Å). Extended Hückel theory[6] and recent ab initio molecular orbital calculations[7] suggest a preference for a concerted transition state. However, the ab initio study by Ha and co-workers[7] was performed assuming that all transition structures had C_s symmetry. However, we found that structure **3** is lower in energy than the transition structure found by Ha (at the same level of theory (UHF/3-21G) used in our calculations) by about 4 kcal/mol. The authors' conclusion

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that the reaction is concerted is also questionable even on the basis of their calculations. The "concerted" calculated transition structure has an unrealistically long C--H breaking bond of 2.05 Å, and a forming O–H bond of 0.99 Å; this length is virtually equal to the O–H bond length in protonated formaldehyde[26] (0.98 Å), suggesting that the hydrogen is already completely transferred to the carbonyl group. Calculation of the harmonic frequencies on Ha's published structure[7] showed that, in fact, there are two negative eigenvalues in the force-constant matrix. Both negative eigenvalues correspond to conformational distortion of the molecule to C_1 symmetry and not to hydrogen transfer. We did not locate a "concerted" transition structure, and it seems unlikely that a concerted pathway could exist along with a stepwise one. We therefore conclude that the mechanism for the rearrangement involves initial hydrogen transfer followed by CC bond cleavage in a subsequent step.

Geometries. In our previous communication[13] we noted that the preference for six-membered transition structures in the intramolecular hydrogen abstraction by alkoxy radicals was the result of a more favorable entropy of activation,[27] rather than an unstrained "chair-like" transition-state geometry, as implied in earlier reports.[2,18b] Indeed, the six-membered cyclic structure strongly resembles a *five*-membered ring of heavy (nonhydrogen) atoms, such as cyclopentane or tetrahydrofuran. The same applies to the other structures in this study. All resemble five-membered rings (Figure 1) having one long C–O "bond". The C--H--O angle is reasonably close to linear (153–157°) except for **3** and **4**, which have the smaller angles of transfer of 144° and 146°, respectively. These slightly smaller values result from the relatively large values for the C=O--H angle in **3** (109°) and C—C--H angle in **4** (106°). These small angles underscore the very early nature of these two transition states.

In the open-shell systems, the extent of hydrogen transfer is proportional to the activation barrier. For example, in **1** and **2**, the C--H and O--H bond lengths are almost identical (**1**: C--H = 1.37 Å, O--H = 1.18 Å; **2**: C--H = 1.35 Å, O--H = 1.19 Å), and so are the free energies of activation (12 and 11 kcal/mol, respectively), while **3**, a much earlier transition state (C--H = 1.24 Å; O--H = 1.40 Å) at the HF/3-21G level, is calculated to have an activation barrier of only 1.6 kcal/mol at the PMP2/6-31G* level. Similarly, **4** is an even earlier transition state (C--H = 1.17 Å; O--H = 1.52 Å) and is lower in energy than the reactant by 11 kcal/mol at the MP2/6-31G*//3-21G level. In agreement with these results, the gas-phase reactions proceed irreversibly.[11,28,29] In contrast, the free energy of activation for the thermal retro-ene reaction of butanal via reaction 5 is the much higher value of 65.7 kcal/mol. This is due to the incipient breakage of the C–C bond and because the reaction is endothermic by 47.5 kcal/mol (uncorrected for zero-point and thermal energies), in part because the less stable enol form of acetaldehyde is formed. The transition structure is later than the other three, with a breaking C--H bond length of 1.41 Å, a forming O--H bond length of 1.21 Å, and a breaking C–C bond length of 2.20 Å. This transition structure is also later than the "parent" retro-ene reaction of 1-pentene.[12b] The parent reaction has a breaking C–H bond length of 1.45 Å and a breaking C–C bond length of 2.11 Å.[12b]

The calculations suggest that the geometric requirements for hydrogen transfer are similar in all four open-shell systems. Structures **1**, **2**, and **4** are almost superimposable, except for the migrating hydrogen atom in **4**, which is a much earlier transition state. Structure **3** differs from **2** in that the carbonyl group is planar in **3**, while it is pyramidalized in **2**. The preference for planarity in carbonyl radical cations and for pyramidalization in the triplet states is known,[30] and such preferences are maintained in the early transition structures **2** and **3**. In contrast to these early transition structures, the necessarily concerted retro-ene reaction of butanal has a drastically different geometry. Structure **5**, which is closer to the products, ethylene and vinyl alcohol, than to butanal, has nearly parallel breaking C--H and C--C bonds ($\omega_{H\text{--}C\text{--}C\text{--}C}$ = 12°), which maximizes overlap of the π orbitals of the developing π-system of ethylene. The almost planar disposition of the atoms of the forming ethylene molecule contrasts with the staggering about C–C bonds which is achieved in the other transition structures. The C--C and forming O--H bonds gain stabilization by overlapping with the π-system of the incipient vinyl alcohol moiety, but this torsional preference would require severely distorted C--C–O and H--O–C angles of attack. As a result, the torsional angles $\omega_{H\text{--}O\text{–}C\text{–}C}$ and $\omega_{C\text{–}C\text{–}C\text{–}O}$ are smaller than 90° (54° and 66°, respectively) as is also the case in the parent ene reaction between propene and ethylene.[12b].

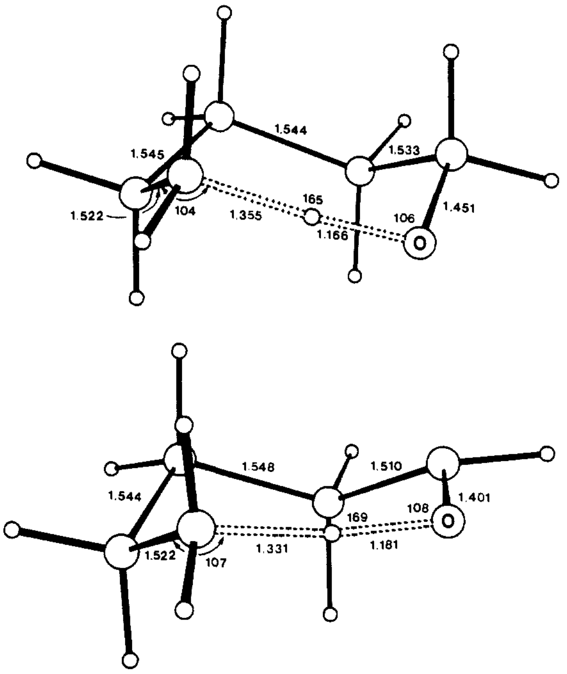

Figure 3. UHF/3-21G transition structures for intramolecular seven-membered-ring hydrogen abstraction by the pentoxy radical and by the triplet state of pentanal.

Six- versus Seven-Membered Transition Structures. In a previous communication,[14] we showed that, in the case of alkoxy radicals, abstraction of a δ-hydrogen atom takes place regioselectively via a six-membered transition state due to entropic factors. Enthalpically, ϵ-hydrogen atom migration through a seven-membered transition state is favored by about 0.8 kcal/mol. In the first step of the Norrish type II cleavage, γ-hydrogen atom transfer is also generally favored (because of different nomenclature, the γ hydrogen of a carbonyl compound corresponds to the δ hydrogen of an alcohol). In order to determine the factors governing the preference for the regioselectivity in the Norrish reaction, the geometries of triplet pentanal and of its hydrogen transfer via a seven-membered transition state were optimized at the HF/3-21G level, and the energies of the optimized structures were calculated at the MP2/6-31G* level. The result is shown in Figure 3, along with the seven-membered-ring transition structure for the hydrogen abstraction in the pentoxy radical.[14] These calculations show that the enthalpy of activation is higher for δ-hydrogen atom migration, by 0.2 and 0.9 kcal/mol at the HF/3-21G and MP2/6-31G* levels, respectively, in contrast to what we found for the corre-

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sponding alkoxy radicals.[13,14] The six-membered transition structure for hydrogen atom migration in the butoxy radical is more strained than the seven-membered cyclic structure; hence the activation enthalpy is lower for the latter. In particular, the H--C-C and H--O-C angles in the six-membered transition structure deviate considerably from the ideal values calculated for the corresponding angles in the *inter*molecular reaction between methoxy radical and methane (see below). Calculations of the steric energies of the two transition states and the respective starting materials, using a modified MM2 force field,[13] confirm that more bending strain is built in the smaller of the two cyclic transition structures. On the other hand, the six-membered transition structure for the rearrangement of triplet butanal is considerably less strained. Force-field calculations[31] yield a preference for abstraction via a six-membered transition state of 0.4 kcal/mol, similar to the HF/6-31G* value. The activation entropy[32] is also less negative (−4.5 eu) than it is for the seven-membered transition state in triplet pentanal (−12.7 eu), leading once again to a marked preference for γ-hydrogen atom migration, as is the case with alkoxy and alkyl radicals.

Most experimental work on the Norrish type II cleavage has been done with aromatic ketones, which have a planar triplet state,[33] so that our calculations on aldehydes may not provide an adequate rationalization for the preference for γ-hydrogen atom abstraction in the reactions of aromatic systems. We thus recalculated the energies of the six- and seven-membered transition structures using the geometries derived from the calculations described above, with the exception of the geometry about the carbonyl carbon, which was constrained to be planar. The six-membered constrained transition state energy was calculated to be 18.6 kcal/mol higher (MP2/6-31G*) in energy than triplet butanal, while the seven-membered constrained transition state was calculated to be 19.9 kcal/mol higher in energy than triplet pentanal. The resulting 1.3 kcal/mol preference for a six-membered constrained state is enthalpic; as described before, entropic factors enhance the preference for the smaller cyclic transition structure.

Distance and Angle Dependence of Rates of Hydration Transfer. We also tested some of the empirical rules that have been suggested by the behavior of certain ketones under photolytic conditions or in the mass spectrometer. For example, Djerassi's "1.8 Å rule"[34] states that the McLafferty rearrangement of ketones having a rigid structure can occur only if the carbonyl oxygen and the migrating hydrogen are less than 1.8 Å apart in the reactant. This implies a maximum distance of 2.9 Å between the oxygen atom and the carbon atom bearing the hydrogen, since an ordinary C-H bond is about 1.1 Å long. The C--O distance in structure **8** is 2.67 Å at the HF/6-31G* level. Nevertheless, stretching the C--O distance by 0.23 Å (to 2.9 Å) resulted in an increase in energy of only 2.1 kcal/mol. By comparison, a 4.1-kcal/mol destabilization results from a 0.2-Å increase in the C--O distance in the transition state for the reaction between hydroxy radical and methane.[13] In other words, transition structure **8** is relatively more "deformable" than that of the alkoxy radical. Inspection of the steroids studied by Derassi suggests that other factors may inhibit hydrogen migration, in addition to alterations of O--H distances. In particular, due to the rigidity of the systems, abstraction by the *in-plane* odd electron on oxygen cannot be achieved. Wagner[35] has suggested a $\cos^2 \tau$ dependence of the rate of reaction, where τ is the C—C=O---H torsional angle. The work of Henion and Kingston[36a] and of Aoyama[36b] shows that the McLafferty rearrangement cannot take place in ketones in which τ is constrained to be 80° or larger. Analogous angular relationships in the reaction between triplet formaldehyde and methane have been analyzed recently by Morrison and coworkers.[37] Their calculations (HF/3-21G) confirm a preference for a transition-state geometry in which the forming O--H bond is nearly in the plane of the formaldehyde moiety; rotating the hydrogen atom out of the plane causes an increase in energy. In our calculated transition structure **7**, one of the H—C=O--H torsional angles is equal to 28° (HF/6-31G*). We have calculated the energy required to alter this angle by 15° intervals. A 90° rotation ($\omega_{\mathrm{H-C=O--H}} = 118°$), which corresponds approximately to abstraction by the odd electron in the half-filled π^*_{CO} orbital, resulted in an energy increase of 9.4 kcal/mol relative to structure **7**. This large preference for abstraction involving the in-plane half-occupied orbital is in agreement with earlier studies by Turro on the relative ease of the two modes of reaction.[38]

Conclusion. The calculations presented in this paper indicate that while the reactions studied all represent essentially the same fundamental type of process, differences in activation energy are related to the differences between closed-shell, open-shell, and charged open-shell systems. This is also reflected by the structural similarities in cyclic transition states **1**–**4**. Regioselective γ-hydrogen atom transfer in the Norrish II cleavage is due to a combination of both enthalpic and entropic factors, both of which favor a six-membered cyclic transition structure over a seven-membered one. In this respect, the reaction differs from the analogous process in alkoxy radicals, where the seven-membered transition state is predicted[14] to be more easily achievable enthalpically but greatly disfavored entropically. Our calculations also indicate, in agreement with experimental results, a clear preference for hydrogen abstraction by the in-plane, half-occupied nonbonding orbital of the triplet aldehyde, rather than the out-of-plane half-occupied π^* orbital.

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