Organic and Biological Chemistry

The Electronic Structure of the Six-Membered Cyclic Transition State in Some γ-Hydrogen Rearrangements

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Abstract: The course of the γ-hydrogen rearrangement in 2-pentanone is followed by nonempirical molecular orbital calculations assuming a six-membered cyclic transition state. Charge density, overlap populations, and energies are calculated for the molecule ion, the neutral molecule, and the n,π* excited species. A rationale is given for the parallel course of the reaction under electron-impact and photochemical conditions, and for the difficulty of inducing reaction in the neutral ground state. The relative merits of stepwise and concerted mechanisms are discussed, the question of whether hydrogen is transferred as H^+, $H\cdot$, or H^- is considered, and alternate transition-state geometries are explored. Calculations are also performed for alternate reaction paths in the consecutive γ-hydrogen rearrangement reaction. Finally, the Appendix discusses the relative merits of two methods of calculating the energies of positive ions by molecular orbital methods.

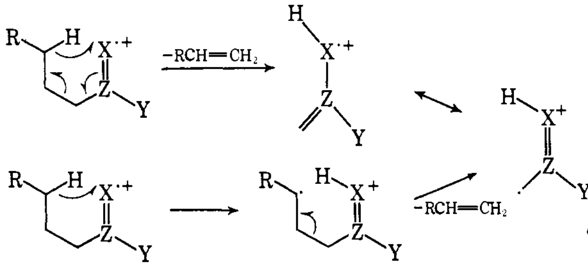
Recent attempts to explain the fragmentation mechanisms of organic molecules under electron impact have been most successful in terms of localization of positive charge at favored sites.[2] These sites most often are heteroatoms from which lone-pair electrons have been removed. The resulting molecular ion is considered to have both a positive charge and a radical localized at the same site, either of which may trigger further decomposition and rearrangement.[3,4]

Rearrangement reactions result in fragment ions which cannot be derived from any simple bond cleavage process in the original molecule ion. The determination of molecular structure by interpretation of the mass spectral fragmentation patterns is considerably complicated by these effects. A large number of rearrangement reactions have been discovered; the most common type involves the transfer of hydrogen with multiple bond cleavage. Among systems of this type, the rearrangement of a γ-hydrogen in aliphatic ketones and their analogs[2] has been the most extensively studied. In mass spectrometry, this reaction has been termed the McLafferty rearrangement.[5,6] Moreover this type of reaction is not restricted to electron-impact systems. For example, a parallel rearrangement reaction, known as the Norrish type II process,[7-9] may be induced photochemically in solution and in the gas phase.

Despite the very substantial number of experimental studies of the γ-hydrogen rearrangement, the questions of whether the reactions proceed *via* stepwise or concerted mechanisms, and whether the transferred entity should be labeled as a proton, a hydrogen radical, or a hydride ion, are still debated.[4a,6,10]

This paper represents an attempt to clarify this uncertain situation by theoretical studies of the electronic structure of the six-membered cyclic transition states generally accepted for these reactions. The molecular orbital approach[11-15] used has the specific advantage of eliminating any hidden assumptions implicit in the localized charge concept.

Studies of mass spectrometric rearrangements of deuterated ketones and esters have established that in these systems only γ-hydrogen atoms are transferred.[6]



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(1) (a) The Dow Chemical Company, Wayland, Mass. 01778. (b) Purdue University, Lafayette, Ind. 47907.

(2) F. W. McLafferty in "Determination of Organic Structures by Physical Methods," F. C. Nachod and W. D. Phillips, Ed., Academic Press, New York, N. Y., 1962, p 117; H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day Inc., San Francisco, Calif., 1967.

(3) F. W. McLafferty, *Chem. Commun.*, 78 (1966).

(4) (a) F. W. McLafferty and T. Wachs, *J. Am. Chem. Soc.*, **89**, 5043 (1967); (b) T. Wachs and F. W. McLafferty, *ibid.*, **89**, 5044 (1967).

(5) F. W. McLafferty, *Anal. Chem.*, **28**, 306 (1956); **31**, 82 (1959).

(6) Reference 2, section 3-7.

(7) W. Davis and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **69**, 2153 (1947).

(8) J. N. Pitts, Jr., and J. K. S. Wan in "The Chemistry of the Carbonyl Group," S. Patai, Ed., Interscience Publishers, New York, N. Y., 1966, pp 841-843.

(9) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965.

(10) G. Spiteller and M. Spiteller-Friedmann, *Monatsh.*, **95**, 257 (1964).

(11) F. P. Boer, M. D. Newton, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **52**, 890 (1964).

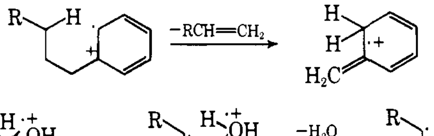
(12) M. D. Newton, F. P. Boer, W. E. Palke, and W. N. Lipscomb, *ibid.*, **53**, 1089 (1965).

(13) M. D. Newton, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 2353 (1966).

(14) F. P. Boer, M. D. Newton, and W. N. Lipscomb, *ibid.*, **88**, 2361 (1966).

(15) M. D. Newton, F. P. Boer, and W. N. Lipscomb, *ibid.*, **88**, 2367 (1966).

The reaction may be visualized as concerted (1) or stepwise[2] (2). The analogous Norrish II reaction proceeds when an n electron on X (carbonyl oxygen) is excited to the π^* orbital.[16–19] In general, the rearrangement favors secondary hydrogens over primary.[20] The postulated mechanisms have been generalized by the use of the structural entities X, Y, and Z. For example, γ-hydrogen rearrangements are observed for X = O, C, N, or S, while Z may be C, N, S, or P. Similarly, Y encompasses a broad range of functional groups.[6,12] This type of reaction also occurs in aromatic systems (3), while similar mechanisms have been proposed to explain rearrangement reactions of saturated functional groups (4).[6,21]



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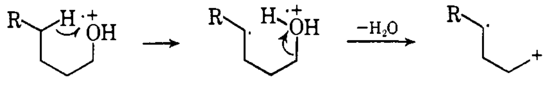
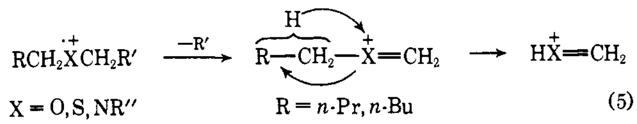


(4)

We note, however, that while odd-electron systems appear to be site specific, utilizing an unpaired electron in a highly directional atomic orbital, many even-electron systems appear to react by an entirely different mechanism. For example, the system



$$\mathrm{RCH_2\overset{\cdot+}{X}CH_2R'} \xrightarrow{-\mathrm{R'}} \mathrm{R{-}CH_2{-}\overset{+}{X}{=}CH_2} \longrightarrow \mathrm{H\overset{+}{X}{=}CH_2}$$

(5)

involves H transfer from all carbon atoms beginning with C_α.[22–24]

Conditions for Rearrangement

Our first task is to postulate the necessary conditions for γ-hydrogen transfer and to identify the reasons underlying the parallel paths taken by the reaction under electron impact and photolytic conditions. Some useful insight toward such understanding can be achieved in terms of the familiar three-orbital Hückel LCAO model. While this model imposes a number of undesirable constraints on the behavior of the system, it has the virtue of simplicity, and many of its features will appear in the fuller molecular orbital treatment presented below.

We begin by considering three atomic orbitals of the reacting system: χ_C, an sp^3 orbital on C_γ; χ_H, a hydrogen 1s orbital; and χ_X, which can be a 2p orbital on carbonyl oxygen, but need not be specified. We also assume that the corresponding diagonal elements of the Hamiltonian matrix, H_{CC}, H_{HH}, and H_{XX}, are equal (to α) and assign appropriate values β for the off-diagonal matrix elements H_{ij}. If we ignore nonorthogonality effects ($S_{ij} = \delta_{ij}$), the secular equations

$$\sum_j C_{jk}(H_{ij} - \epsilon_k S_{ij}) = 0$$

readily yield eigenvalues, ϵ_k, and eigenvectors, $\psi_k = \Sigma C_{jk}\chi_j$, for the molecular orbitals of the system.

Initially (Figure 1a), the system contains two electrons in the C–H orbital ψ_1 at $\epsilon_1 = \alpha + \beta_1$ (where $H_{CH} = \beta_1$ is the C–H bond integral); a single electron (for ionic and excited species) in the oxygen nonbonding orbital ψ_2 at $\epsilon_2 = \alpha$; and an unoccupied σ^* orbital ψ_3. In the transition state (Figure 1b), the hydrogen atom is placed between C and X such that $H_{CH} = H_{HX} = \beta_2$. The lowest MO ψ_1 is now a three-center bonding orbital analogous to B–H–B bridge bonds found in boron hydrides,[25] while the nonbonded MO ψ_2 has a node at the hydrogen atom with the unpaired electron shared between C and X. The eigenvalues depend in an important way on the magnitude of the C–X interaction ($H_{CX} = \beta_3$) as shown in Figure 2. In the limit $\beta_3 = 0$, ψ_2 remains nonbonding with $\epsilon_2 = \alpha$, while the bonding orbital ψ_1 has energy $\epsilon_1 = \alpha + \sqrt{2}\beta_2$. For $\beta_3 < 0$, repulsion between C and X lobes of opposite sign gives increasing antibonding character to ψ_2, while ψ_1 is further stabilized. Thus, for the case $\beta_3 = \beta_2$, ϵ_2 takes on the value $\alpha - \beta_2$, while ϵ_1 goes to $\alpha + 2\beta_2$. In fact we may expect a transition state between these two limits: for the 2-pentanone geometry discussed below the magnitudes of the overlap integrals suggest that $\beta_3 \sim 0.4\beta_2$ for a C···O distance of 2 Å. The MO's of the final state, defined by complete hydrogen transfer to X (Figure 1c), formally resemble those of the starting system: one electron is now in a carbon nonbonding orbital at $\epsilon_2 = \alpha$, while two electrons form the X–H σ bond at $\epsilon_1 = \alpha + \beta_4$, where β_4 is the X–H bond integral.

These observations suggest the following hypothesis. *The removal of an electron from the four-electron C–H···:X system is a necessary condition for γ-hydrogen transfer with a low activation energy.* We have seen that delocalization of an electron pair over three centers instead of two tends to lower the energy of the bonding orbital γ_1, and thus favors formation of the transition state. However, the energy of ψ_2 will simultaneously be raised. If ψ_2 is singly occupied these effects may approximately cancel and the transition state will be energetically accessible. But, if ψ_2 is doubly occupied, the antibonding terms will be much larger, giving a substantially greater activation energy for rearrangement.[26]

The close parallel between the Norrish II photoelimination of olefins from ketones and the McLafferty rearrangement is then attributed to the fact that both systems provide a mechanism for the removal of an electron, in the former case by excitation to the carbonyl π^* orbital, and in the latter by ionization. Moreover, our hypothesis has an important corollary in the pho-

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[16] J. W. Krans and J. G. Calvert, *J. Am. Chem. Soc.*, **79**, 5921 (1957).

[17] P. Ausloos, *J. Phys. Chem.*, **65**, 1616 (1961).

[18] E. J. Baum, J. K. S. Wan, and J. N. Pitts, Jr., *J. Am. Chem. Soc.*, **88**, 2652 (1966).

[19] C. H. Niod and J. G. Calvert, *ibid.*, **89**, 1790 (1967), and references cited therein.

[20] H. Budzikiewicz, C. Fenselau, and C. Djerassi, *Tetrahedron*, **22**, 1391 (1966).

[21] F. W. McLafferty "Interpretation of Mass Spectra," W. A. Benjamin, Inc., New York, N. Y., 1966.

[22] C. Djerassi and C. Fenselau, *J. Am. Chem. Soc.*, **87**, 5747 (1965).

[23] S. D. Sample and C. Djerassi, *ibid.*, **88**, 1937 (1966).

[24] C. Djerassi and C. Fenselau, *ibid.*, **87**, 5752 (1965).

[25] W. H. Eberhardt, B. C. Crawford, and W. N. Lipscomb, *J. Chem. Phys.*, **22**, 989 (1954).

[26] Examples can occur under pyrolytic conditions. The four-electron alkyl acetate system eliminates ethylene in the gas phase but the reaction requires temperatures of the order of 400° due to the very high activation energy of 45 kcal/mol [A. Maccoll, *J. Chem. Soc.*, 3398 (1958); see also E. D. Hughes and C. K. Ingold, *Quart. Rev.* (London), **6**, 34 (1952)].

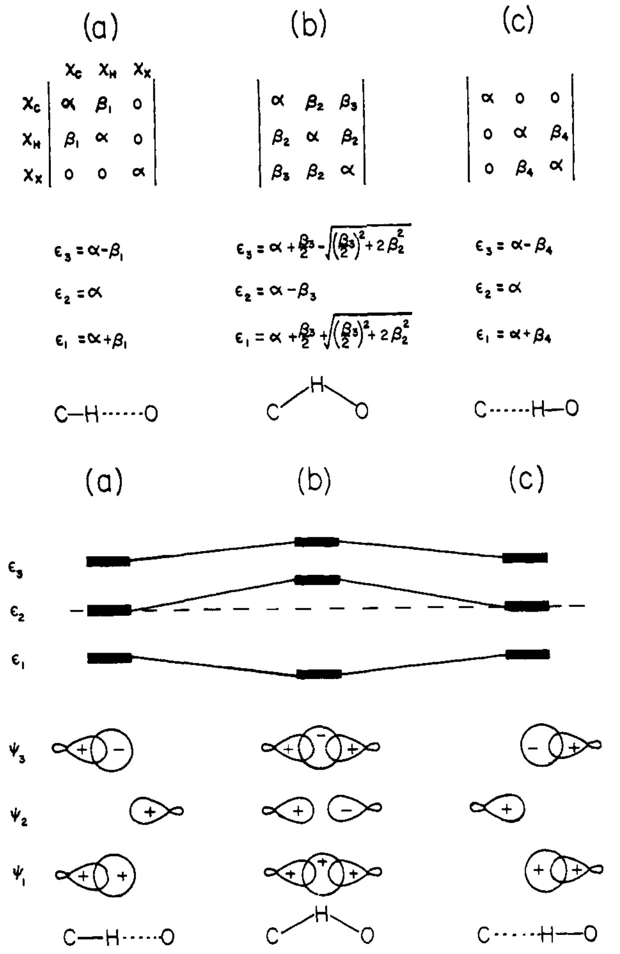
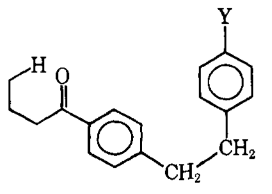


Figure 1. (upper) Hamiltonian matrix elements and the resulting eigenvalues from the Hückel three-orbital model. (lower) Wave functions and energies from the Hückel three-orbital model. Sections a, b, and c refer to initial, transition, and final states, respectively, for H transfer between C and X.

tolysis of ketones: the carbonyl π^* orbital, which is orthogonal to the C–H–X plane, should not participate appreciably in the reaction, but functions only as a sink for the fourth electron. Evidence that the Norrish II process can occur from either the singlet or the triplet state is not, therefore, altogether surprising.[27]

The opposite side of this coin is, of course, the conclusion that γ-hydrogen rearrangements should not occur in four-electron systems. The absence of reaction from the ground state of neutral ketones furnishes a trivial example.

A more interesting case is provided by recent observations of the elimination of ethylene from *para*-substituted butyrophenones.[4b] Although the *p*-amino substituent should have only a small effect on the elimination of ethylene, the change from I to II causes a dramatic decrease in the M − 28 ion abundance. The substantially lower ionization potential of the amino moiety is sufficient to cause localization of the charge and radical site in the aminobenzyl group.[28] Thus the γ-hydrogen high-energy rearrangement must proceed through the four-electron transition state and is not observed.



I, Y = NO_2
II, Y = NH_2

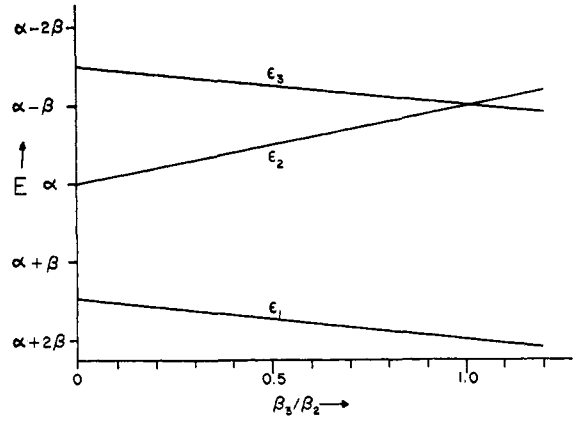


Figure 2. Variation of the eigenvalues of the three-orbital system as a function of the C–X "bond" integral (β_3).

This model suggests that the energy barrier in the transition state for γ-hydrogen rearrangements is associated with antibonding character in the molecular orbital ψ_2. Therefore, any effect tending to reduce the energy of this orbital should enhance the rate of reaction. Atomic orbitals of the substituent group Y can mix with those of ψ_2 of our limited three-orbital system, and, when Y is electron withdrawing, can be expected to lower the energy of this orbital by providing favorable alternate sites for the unpaired electron with respect to the relatively antibonding C–H–X region. Such a condition is equivalent to inclusion of resonance forms where the odd electron is localized on the electron-withdrawing group. This prediction has been corroborated experimentally in a series of substituted butyrophenones where a relatively high ρ value of +2.0 has been observed.[4a]

The Mechanism of Rearrangement in the 2-Pentanone System

The preceding observations, while providing a useful framework for discussion, leave some critical questions unanswered. Because only three orbitals have been considered, we have no way to distinguish between the concerted and the stepwise mechanisms (eq 1 and 2) for eliminating the olefin fragment. Furthermore, the limited nature of the model seriously restricts the form of our wave function. For example, the transferred entity has been virtually defined to be a hydrogen radical since a large calculated net charge on H can be obtained only by making drastic assumptions about the magnitudes of the matrix elements α and β. Fuller consideration of the model also requires calculations on a series of alternative transition-state geometries, although the many degrees of freedom of the system

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[27] P. J. Wagner and G. S. Hammond, *J. Am. Chem. Soc.*, **87**, 4009 (1965).

[28] G. A. Junk and H. J. Svec, *ibid.*, **89**, 790 (1967), have reported evidence that the ionization potential of a polyfunctional molecule is determined by the functionality of lowest ionization potential.

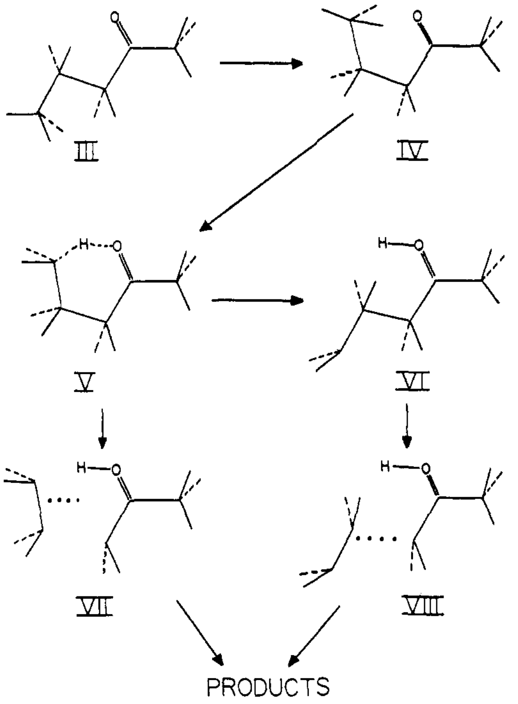

Figure 3. Molecular geometries used for the detailed calculations on 2-pentanone. Two alternate paths for the elimination of olefin are given, one directly from the transition state V, and the other from the product species VI after H has been transferred to O.

put a practical constraint on the number of computations.

These considerations have prompted us to undertake detailed molecular orbital calculations on an explicit system of chemical significance. While this approach lacks the generality of our previous discussions, it has the advantage of giving us reasonably objective criteria in the critical matter of estimating our matrix elements. The method used,[11-15] moreover, includes all the electrons and all the atomic centers of the reacting system, and the orthogonality assumption is not invoked in the solution of the secular equations. As a result, many of the previous limitations on the form of the wave function have now been removed. In our method, the overlap and kinetic energy integrals between all atomic orbitals in the system are evaluated exactly. Parameters for constructing the Hamiltonian matrix are derived from self-consistent field calculations on appropriate model compounds. These parameters are the diagonal elements H_{ii} (or γ's) and coefficients K used in a modified Mulliken approximation to estimate the potential energy parts of the off-diagonal elements H_{ij}. Existing SCF calculations on formaldehyde[29] and a number of small hydrocarbons[30] make good models for ketone systems, and the transferability of these numbers from model to test molecules has now been amply discussed and documented.[15] In addition, computations by this method on boranes[14] have demonstrated the validity of this parametrization for three-center bonded systems. Since the earlier studies[13] indicated that α's and K's for unsaturated atoms tend to be anisotropic, we have taken the precaution of performing two sets of calculations (assuming isotropic and anisotropic parameters). Happily our results were, with minor exceptions, insensitive to this choice, and the results quoted will refer to the less arbitrary isotropic set.

Two precautionary comments are in order. Because the wave functions and Hamiltonian are now iterated to self-consistency in this method, exaggeration of calculated net charges may occur in certain instances. Also, although the molecular parameters used are chosen to give the correct magnitude of the Hamiltonian matrix elements at normal (equilibrium) bond distances and angles, the form of our approximation does not guarantee the correct functional dependence of energy on all distances and angles, or even that the energy is minimized at the experimental geometry. For this reason, and because the calculated energies are only approximate (see Appendix), we compare here only those energies calculated at normal bond distances and angles, for which the parameters are believed to be correct.

2-Pentanone was chosen as our model reacting species. A planar transition state is reached in two simple steps (Figure 3). First, rotation about the C_α–C_β bond brings C_γ from its initial coordinates (III) to a point 2.0 Å from the oxygen atom. In this configuration (IV), the carbon and oxygen atoms all lie in a plane, while two of the three γ-hydrogens are equidistant (about 1.6 Å) from oxygen, above and below this plane. In the second step, a 60° rotation about C_β–C_γ brings one of the γ-hydrogens into the reaction plane about 1.1 Å from the carbonyl oxygen. While this configuration can be achieved without any angle strain in the six-membered ring, examination of a series of activated complex geometries showed that maximum bonding occurs when the ring angles are opened up by a small amount (about 15°). In this configuration, the H atom is about 1.3 Å from C and 1.2 Å from O. This result is in accord with the observation that the hydrogen-bond distances in boron hydrides are somewhat longer for bridge than terminal hydrogens. In the final step (VI), C_γ swings away leaving H bonded to oxygen.

The form of the highest filled molecular orbital $\psi_n = \psi_{24}$ is of considerable interest because of its extensive changes in structure and energy during the course of the reaction. (Here n represents the number of electron pairs in the neutral molecule.) We shall see that this molecular orbital can be closely identified with the nonbonding MO ψ_2 from our previous Hückel analysis. The behavior of ψ_n along the reaction coordinate is illustrated schematically in Figure 4, while its electron density[31] is given in Table Ia. In the neutral ketone in its normal geometry (III) much of the electron density of ψ_n is localized on oxygen, although some spreading of charge over the remainder of the σ system occurs. This situation agrees qualitatively with the chemist's usual notion that the oxygen lone-pair electrons are the ones excited or ionized, even though lone pairs as such are not completely isolated as individual MO's in calculations of this type.[32] As the reaction proceeds to geometry IV, significant electron density builds up on C_γ and on the two γ-hydrogen atoms that are nearest to the carbonyl group, with the phase of the wave

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[29] M. D. Newton and W. E. Palke, *J. Chem. Phys.*, **45**, 2329 (1966).

[30] W. E. Palke and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 2384 (1966).

[31] R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2238, 2343 (1955).

[32] R. Hoffmann, *ibid.*, **40**, 2745 (1964).

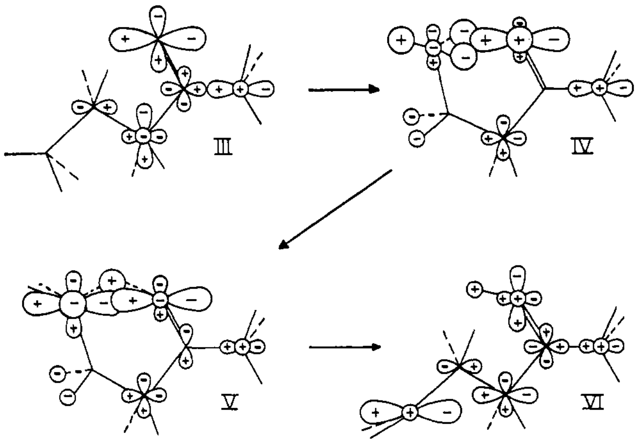


Figure 4. Schematic drawing of the wave function of the highest filled molecular orbital of 2-pentanone during the transfer of γ-hydrogen. The s and p orbitals are scaled according to their coefficients in the wave function. Coefficients smaller than 0.15 are not indicated, with the exception of H_γ in V, which is drawn oversize (the actual coefficient is only 0.031) simply to indicate its phase.

function on oxygen opposite in sign to that on carbon and the hydrogen atoms. Since the hydrogen–oxygen distances are now well below the van der Waals contact limit, the energy of this MO, ϵ_n, is raised substantially by the resulting electronic repulsions (see Figure 5). Rotation of the terminal methyl group by 60° induces an even more dramatic change in the wave function. One of the γ-hydrogens is now slightly closer to oxygen than to carbon, and in fact has just passed through the node of this nonbonded orbital. The coefficient on hydrogen is small, of the same sign as on oxygen, and opposite to that on carbon. The electron density is seen (Table Ia) to be almost evenly divided between C_γ and O, slightly favoring C_γ, but with no appreciable value on H itself. The electronic repulsion associated with this MO, as measured by ϵ_n, now reaches its maximum. As C_γ swings away from the oxygen atom, leaving H bonded to O, the radical character of the molecule ion, which was originally concentrated on the carbonyl oxygen, continues to flow smoothly over to C_γ, while the energy ϵ_n decreases. We observe, however, that some density remains distributed at C_γ and at O.

Table I

(a) Charge Density in the Highest Filled Molecular Orbital of 2-Pentanone[a,b]

	III	IV	V	VI
C(1)	0.16	0.09	0.09	0.06
C(2)	0.06	0.01	0.02	0.07
C(3) = C_α	0.19	0.05	0.10	0.18
C(4) = C_β	0.01	0.00	0.01	0.05
C(5) = C_γ	0.01	0.09	0.37	0.45
O	0.52	0.48	0.35	0.12
H(1)	0.00 (3)	0.00 (3)	0.00 (3)	0.00 (3)
H(3) = H_α	0.00 (2)	0.00 (2)	0.00 (2)	0.00 (2)
H(4) = H_β	0.00 (2)	0.01 (2)	0.03 (2)	0.01 (2)
H(5) = H_γ	0.01 (3)	0.09 (1) 0.08 (2)	0.00 (2) 0.00 (1)	0.00 (2)
H(O)	...	...	...	0.01 (1)

(b) Net Charge on the 2-Pentanone Molecule-Ion[b]

	III	IV	V	VI
C(1)	−0.23	−0.32	−0.29	−0.28
C(2)	+0.71	+0.64	+0.67	+0.74
C(3) = C_α	+0.04	−0.11	−0.08	+0.02
C(4) = C_β	+0.07	+0.03	+0.04	+0.17
C(5) = C_γ	−0.21	−0.11	−0.44	−0.79
O	+0.07	+0.18	+0.24	+0.40
H(1)	+0.09 (3)	+0.08 (3)	+0.09 (3)	+0.10 (3)
H(3) = H_α	+0.05 (2)	+0.05 (2)	+0.05 (2)	+0.05 (2)
H(4) = H_β	+0.01 (2)	0.00 (2)	+0.03 (2)	+0.01 (2)
H(5) = H_γ	+0.05 (3)	+0.02 (1) +0.16 (2)	+0.07 (2) +0.30 (1)	+0.10 (2)
H(O)	...	...	. ...	+0.18 (1)

[a] Assuming occupation by one electron. [b] Multiplicities of the atoms are given in parentheses.

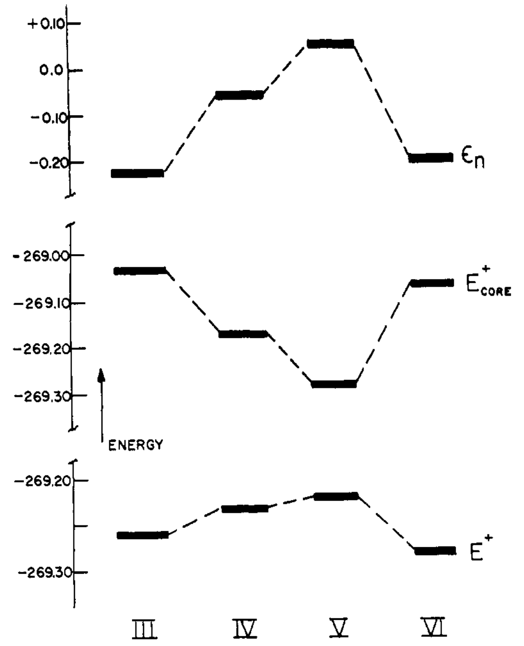


Figure 5. Energy terms for the γ-hydrogen rearrangement for the 2-pentanone molecule ion. The terms are defined in the Appendix.

The effect of the three-center bonding orbital ψ_1 of our simple Hückel model is more difficult to isolate when we consider the full 40-orbital 2-pentanone molecule, because this bond is not associated with any particular eigenvector, but is rather spread variously among the lowest 23 filled molecular orbitals. However, its net effect in the assumed transition state (V) can be inferred from the Mulliken overlap populations[31] computed from the MO coefficients (Table II). Likewise, the energy of this bond cannot be associated with any particular eigenvalue. In the Appendix, we show that this energy can be isolated in the quantity E^+_{core} (Figure 5), although this term probably underestimates the amount of stabilization conferred by delocalization of the bonding electrons over three centers instead of two because E^+_{core} also implicitly includes the nuclear repulsions.

Table II. Mulliken Overlap Populations for the 2-Pentanone Molecule Ion[a]

	III	IV	V	VI
H_γ–C_γ	0.73	0.64	0.32	0.00
H_γ–O	0.00	0.02	0.33	0.53
O–C (carbonyl)	0.94	0.92	0.96	1.05
C_α–C_β	0.86	0.85	0.83	0.83

Some of the energy terms relevant to the γ-hydrogen rearrangement of 2-pentanone for neutral, ionic, and excited species are given in Table III. The reader is referred to the Appendix for discussion and definitions of these quantities. For the neutral ketone, the large electronic repulsive forces associated with the highest filled molecular orbital, taken together with an increase in the nuclear repulsive terms, give rise to a very unfavorable transition state, calculated to be about 200 kcal (undoubtedly overestimated), above the energy of the ketone in its normal geometry. Clearly, this situation can be relieved considerably by removal of one of the two repelling electrons in this MO. When this electron has been removed, say by electron bombardment to give the molecule ion, the calculated activation energy E^+(III) − E^+(V) for the system is 18.9 kcal, which may be compared to an experimental estimate[33] of ≥10 kcal. Because the energy of the system was not completely minimized with respect to its geometrical parameters, we would expect our calculated activation energy to be on the high side in any case. The energy, E^+, of the 2-pentanone molecule ion is plotted along the reaction coordinate in Figure 5, together with its component terms ϵ_n and E^+_{core}. The energetics for the 2-pentanone n,π^* excited state are very similar to the ionic case, since the orthogonality of the carbonyl π^* orbital to any atomic orbitals lying in the reaction plane leaves the energy of this MO, ϵ_{n+1}, essentially unchanged during the course of the reaction. The calculated activation energy E^*(III) − E^*(V) = 19.4 kcal is again somewhat higher than the experimental value,[19] believed to be in the vicinity of 5 kcal, but is generally reasonable.

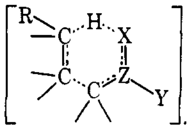
Table III. Energies[a] in Atomic Units for the γ-Hydrogen Rearrangement of 2-Pentanone

	III	IV	V	VI
ϵ_{n+1}	+0.0623	+0.0521	+0.0615	+0.0626
ϵ_n	−0.2233	−0.0603	+0.0515	−0.2168
E^+_{core}	−269.0354	−269.1749	−269.2792	−269.0651
E^+	−269.2587	−269.2352	−269.2277	−269.2819
$E^{*\,b}$	−269.1964	−269.1831	−269.1662	−269.2193
E^0	−269.4820	−269.2955	−269.1762	−269.4987

[a] For a definition of these symbols, see Appendix. Values of ΣE_i^a used in defining the energies are H, −0.250; C, −25.241; and O, −51.770 from atomic wave functions of E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963). [b] For a comment on the value of E^* see T. Koopmans, *Physica*, **1**, 104 (1934).

Concerted *vs.* Stepwise Mechanism

The problem of concerted *vs.* stepwise elimination of the olefin from the molecule has not yet commanded our attention. With the provision that the equilibration between the two tautomeric forms of the product ion is rapid, the concerted mechanism may be defined by the formation of a transition state with an electronic structure pictured[8] as



The above formulation, which is essentially independent of whether a proton or a hydrogen atom is transferred, requires the simultaneous formation of the X–H bond and the scission of the bond between C_α and C_β.

The detailed calculations on the 2-pentanone system show unambiguously that such a transition state does not occur. The overlap populations for the transition state V (Table II) indicate no weakening of the C_α–C_β bond. In addition, no increase is observed for the C_α–Z or C_β–C_γ overlap populations, nor is there any diminution of the X–Z double bond. We note that essentially different atomic orbitals are being used to form the various bonds from a given center, and we do not have the condition for a true aromatic system. Thus, complete electron delocalization within the cyclic transition state cannot reasonably be expected. The apparent lack of evidence from the overlap populations for incipient ethylene formation may in part reflect the absence of strain in the six-membered transition state.

The transfer of hydrogen appears to precede elimination of ethylene, and therefore the over-all reaction should be considered to occur *via* a stepwise mechanism. After the hydrogen has been transferred, free rotation can again occur about the C_α–C_β bond. However, the lack of any significant decrease in the C_α–C_β overlap population in VI precludes the possibility that removal of the C_α–H or C_α–X interactions somehow induces olefin elimination. Ejection of the olefin fragment is nevertheless a facile reaction in these systems. Calculations were performed for geometries VII and VIII (Figure 3) where the elements of ethylene were removed over a series of increasing distances from both the transition state V and the intermediate product VI. The electron density of the unpaired electron in ψ_n was found in each case to increase smoothly at C_α and O, at the expense of C_γ. Finally at infinite separation the unpaired density is completely localized on the $C_3H_6O\cdot^+$ fragment. Thus, the driving force for olefin elimination appears to be the creation of a more favorable radical site rather than the appearance of any markedly antibonding regions in the ion VI formed after γ-hydrogen transfer. Unfortunately, the qualifications about the effects of distance variation on energy cited above preclude reliable estimates of the activation energies of concerted transition states where the C_α–C_β bond is stretched. This question should be explored further when exact SCF calculations on systems of this size become feasible. What evidence we have suggests that although VI is somewhat more stable than V, neither must surmount a further energy barrier to eliminate the olefin fragment. The excess vibrational energy in the molecule ion may be sufficient to rupture the C_α–C_β bond within the time of a few vibrations.

Studies of this rearrangement in a variety of molecules indicate that the olefin-containing fragment competes with the heteroatom fragment for the positive charge on

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(33) The heats of formation of the $C_6H_{10}O$ and C_3H_6O ions in 2-pentanone are calculated to be 152 and 149 kcal/mol, respectively, by ionization and appearance potential measurements obtained with the photoionization technique [E. Murad and M. G. Ingraham, *J. Chem. Phys.*, 40, 3263 (1964)]. Combining these values with $\Delta H_f(C_2H_4)$ results in a calculated heat of reaction of 10 kcal/mol for the elimination of ethylene from 2-pentanone. An estimate of the enthalpy change of this reaction may also be made for the neutral case. The heat of enolization of approximately 12 kcal [M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, E. A. Smith, and W. E. Smith, *J. Am. Chem. Soc.*, **60**, 440 (1938)] allows us to estimate $\Delta H_f(CH_3COHCH_2)$ as −40 kcal/mol. Thus, the energy is ≥37 kcal/mol for the loss of ethylene from the neutral ketone.

cleavage of the α–β bond.[21,34] Thus, in the mass spectrum of γ-phenyl-2-pentanone the styryl ion, $C_8H_8\cdot^+$, is more abundant than the complementary rearrangement ion, $C_3H_6O\cdot^+$, because the charge is stabilized on C_γ; note, however, that this should also increase the electron density in the antibonding orbital, and thus decrease the total abundance of the rearranged ions.

In summary, the calculated overlap populations suggest a stepwise mechanism, where the formation of the X–H bond appears to be rate determining, after which the system reacts rapidly to eject olefin. No particular stability is implied for enolic species such as VI, which probably have only a transient existence.

Planar *vs.* Nonplanar Transition States

A number of approaches to transition-state geometries besides the planar conformation (V) assumed above may be postulated. Although the system has far too many degrees of freedom to be explored completely, we have examined a number of alternate pathways.

For example, the 4-kcal additional energy associated with eclipsed hydrogen atoms in V can be eliminated by choosing a configuration (Figure 6, top) in which C_γ, H_γ, C(2), and O are coplanar, but C_β is above the reaction plane. However, while this conformation keeps all H atoms staggered, we may have to pay a price in angle strain since H_γ comes no closer than 1.81 Å to oxygen if normal bond distances and angles are assumed. The wave function for this conformation differs little from that of V, and the calculated energy $E^+ = -269.2406$ au is also roughly the same at similar O–H distances

Other variant geometries can be constructed where H_γ approaches oxygen from *above* the plane [C(1), C(2), C_α, O]. One such geometry (Figure 6, bottom) can be obtained from V by rotating the propyl chain by an angle, τ, about the C(2)–C_α bond, while maintaining the eclipsed conformation of the chain as τ increases from zero the hydrogen 1s orbital will begin to mix with the π orbital on oxygen as well as with the lone-pair orbital. Apparently, the π orbital is not available for three-center bonding to hydrogen, since the energy, E^+, increases to 31.7 kcal for $\tau = 22.5°$ and 76.3 kcal for $\tau = 45°$ above the energy for V ($\tau = 0$). (These energies may again be overestimated.) The H_γ–O overlap populations reflect this trend, decreasing from 0.33 ($\tau = 0$) to 0.29 ($\tau = 22.5°$) and to 0.15 ($\tau = 45°$).

Our calculations thus strongly support a planar transition state, at least insofar as the γ-hydrogen mixes exclusively with a lone-pair orbital on oxygen. However, some nonplanarity within the propyl group may be permitted. We note also that the interatomic distances in these geometries appear to be sufficiently large to preclude significant direct interaction between the oxygen orbitals and the C_α–C_β bond.

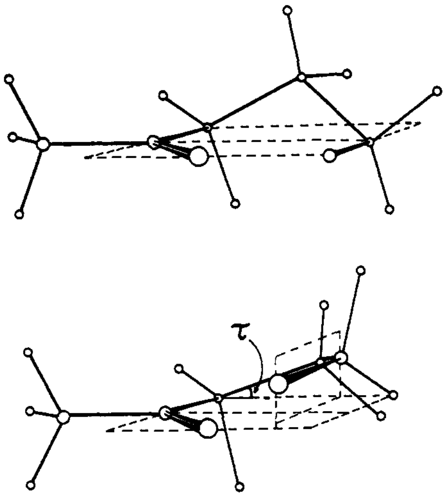
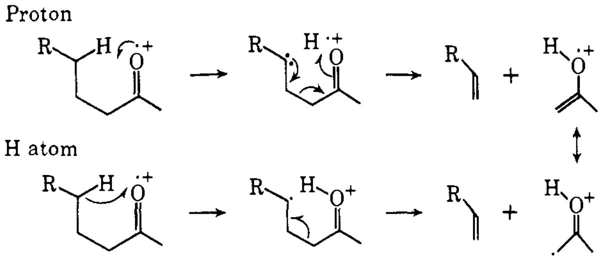


Figure 6. Nonplanar conformations. The top conformation is generated by assuming the plane H_γ, C_γ, C(2) to be normal to O, C(2), C(1). C_β is staggered with respect to C_γ, and C_γ with respect to C_β. In this conformation H_γ is 1.81 Å from O. The lower conformation is constructed by rotating the C_β, C_γ, C(2) plane by an angle, τ, to the C_γ, C(2), O plane. C_γ and C_β, and C_β and C_γ, are eclipsed.

Proton *vs.* Hydrogen Atom Transfer



A number of authors[4a,6,10] have devoted their attention to the question of whether the moiety transferred in the γ-hydrogen rearrangement should be regarded as a proton, a hydrogen atom, or a hydride ion. Mechanisms requiring hydride ion migration[10] have never received serious support, and in any case may be finally dismissed on the basis of the calculated net charges found in the transition state V (Table Ib). A review of the differences between the proton and H atom transfer models is instructive. The proton-transfer model assumes heterolytic cleavage of the C_γ–H bond, and is expected to leave high residual negative charge on C_γ and a high positive charge on H. The initial one-electron bond between oxygen and hydrogen will be weak, but is expected to be further stabilized by the subsequent electronic reorganization when the olefin is eliminated. The unpaired electron in this model presumably is localized on oxygen. In the case of hydrogen atom transfer, no formal charge is expected on either the hydrogen or the γ-carbon (homolytic cleavage), and the latter atom becomes the radical site. In view of the controversy centered on these two models, we feel that a quote[35] from Ingold and Hughes on the subject of intramolecular rearrangements is well worthwhile. "They proceed through a cyclic transition state, and, in such circumstances, it is never possible to determine which way the electrons move during reaction, or even whether they move heterolytically in pairs, or homolytically by uncoupling and recoupling of the pairs. Indeed, the uncertainty principle teaches that the denying of this knowledge to us is one of Nature's ways of making the cyclic transition stage as stable as it is, and thus of enabling the intramolecular reaction

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(34) F. W. McLafferty, "Mass Spectrometry of Organic Ions," Academic Press, New York, N. Y., 1963, p 127.

(35) See Hughes and Ingold, ref 26.

to go as easily as it does. Accordingly, it is unphysical to try to classify intramolecular rearrangements as exclusively electrophilic or nucleophilic, or even as heterolytic or homolytic: if they are typically intramolecular they will have all these characters, though cases may arise in which one character seems to predominate."

The LCAO-MO method, although lacking the intuitive appeal of arrow diagrams, avoids such constraining assumptions on the location or flow of electrons during the course of the reaction. Instead, the wave function is constructed over molecular orbitals, which, for the neutral molecule, are doubly occupied, and which may be delocalized over the entire system. A further advantage of the MO approach is its usefulness for locating an unpaired electron. If, for example, one electron is removed from the highest filled molecular orbital by ionization, this MO then defines the radical character associated with the molecule ion. The unpaired density need not be localized on a single site. In the 2-pentanone system (Table Ia), we have seen that the radical density, which was initially largely at oxygen, shifted over to the γ-carbon as the reaction proceeded. In the assumed transition state, the calculated probability that the radical is localized at C_γ was 0.37. Since alkyl substitution generally stabilizes an unpaired electron, the MO model indicates that the transition-state energy barrier for γ-hydrogen transfer should be lower for secondary, as opposed to primary, hydrogens. This conclusion accords with the chemist's conventional wisdom on this matter, and is in agreement with experimental observations[20] that rearrangements involving secondary hydrogens predominate by a factor of 10 over those for primary hydrogens in both the ionic and photochemical cases. From the point of view of unpaired density, the H atom transfer picture appears to fit the MO and the experimental results reasonably well, while the proton transfer picture apparently has the unhappy feature of placing the unpaired electron on oxygen. Because an O–H bonding orbital should lie at lower energy than a lone-pair orbital on carbon, we would in any case expect the former of these orbitals to be doubly occupied when three electrons are available, and the latter singly. The requirement of the proton transfer model that the lone electron reside on oxygen seems chemically untenable.

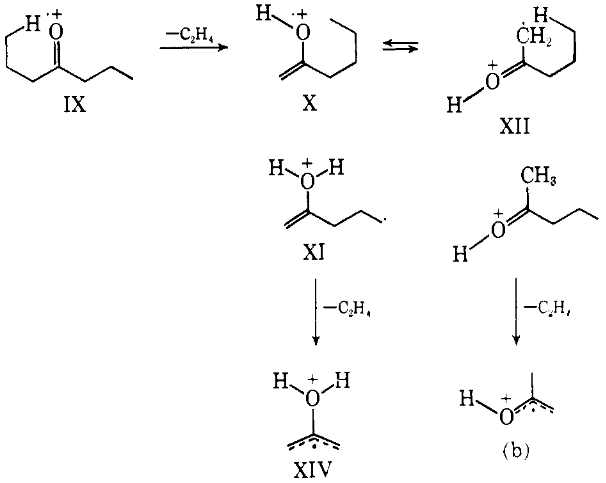
A shift of our point of view to the over-all net charges (Table Ib) is, however, quite instructive. The γ-carbon atom shows a high net negative charge (-0.44) in the transition state, while the hydrogen atom bears strong positive charge ($+0.30$). Furthermore, as the reaction proceeds to geometry VI, C_γ acquires even more negative charge (-0.79). These figures partially support a proton transfer model where heterolytic cleavage results in large residual net charges. We note that this model does not require migration of a proton to a positively charged oxygen. Even though the ionized electron was largely stripped from the oxygen, this atom remains nearly electrically neutral by virtue of its ability to withdraw charge from the carbonyl carbon. (The observed dipole moment of 2.7 D is consistent with a classical C^{+}–O^{-} charge separation of about 0.5 electron in 2-pentanone, which agrees well with our calculated net charges of -0.45 on oxygen and $+0.65$ on carbon for the neutral molecule.) We also note that the development of large net charges, which tend to support a proton transfer picture, were not observed in our Hückel three-orbital model, which seriously oversimplified the mechanistic problem by ignoring the electronic effects occurring in the remainder of the system.

In this instance, the MO wave function reconciles apparently contradictory features of the two mechanistic models cited above in a way that accounts for most of the experimental evidence. We conclude that a forced choice between proton and hydrogen atom transfer may be simplistic. In general, methods of moving electrons about a system by arrow diagrams, although offering valuable insight into mechanism, do not always adequately represent physical reality, and may mask the complex behavior of the wave function in intramolecular rearrangements.

The Consecutive γ-Hydrogen Rearrangement

Molecules containing two sets of γ-hydrogens, for example, dialkyl ketones, exhibit relatively intense peaks in their mass spectra corresponding to the loss of two molecules of ethylene.[6] These peaks arise from the consecutive rearrangement of two γ-hydrogens. Because there are two possible canonical forms of the product ion of a single γ-hydrogen transfer, the mechanistic variations of the second transfer are increased. The most reasonable possibilities are presented in Scheme I. In accord with previous discussion, no attempt has been made to indicate the detailed mechanism of electron flow as the hydrogen is transferred. The approach to the transition state and the transfer of a γ-hydrogen in the above scheme was carried out in an identical manner as in the 2-pentanone case (Figure 3). In both geometries X and XII, the γ-hydrogen was within 1.0 Å of the atom to which it would be transferred.

Scheme I



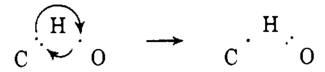
The electronic structure of the transition state X closely reproduces that for the first hydrogen transfer (V). In particular, a high positive charge is again found on the hydrogen being transferred, while negative charge accumulates on the γ-carbon atom. The O–H overlap population increase from zero in IX to 0.19 in X and 0.58 in the intermediate product oxonium ion XI. The existing O–H bond is, however, only slightly perturbed by the approach of the γ-hydrogen, as shown by its overlap populations of 0.51 for IX, 0.49 for X, and 0.59 for XI. Again, no weakening of the C_α–C_β bond was observed. While no attempt was made to remove the elements of the ethylene from geometry X, we have assumed that such calculations would again parallel the 2-pentanone case. Under the set of definitions given previously, this reaction also appears to proceed by a stepwise mechanism.

The energy required to reach the transition state X is essentially zero within the accuracy of these calculations. The controlling factor for this reaction is most likely the entropy difference between the open-chain and cyclic intermediate conformations.[36] The intermediate product XI is calculated to be considerably more stable than the starting species, reflecting the comparative case of forming three bonds to oxygen in an oxonium ion.

The alternate path involving transfer of a γ-hydrogen to the terminal methylene carbon (geometry XII) has also been studied. In this case, the results are quite different. Although the γ-hydrogen again becomes positively charged in the transition state XIII, no incipient bond formation between the γ-hydrogen and the radical site is observed. In addition, the calculated energy of XII is about 20 kcal higher than for the alternate transition state X, suggesting that this reaction path will not be favored. Thus, the most likely product of the consecutive γ-hydrogen rearrangement is product ion XIV, a symmetric oxonium ion with allylic stabilization of the unpaired electron. This result is in accord with recent work[37] characterizing the *m/e* 58 ion in 4-alkanones by means of metastable properties.[37b]

Summary

These results appear to clarify the two main mechanistic questions concerning this rearrangement. Our calculations provide no support for a mechanism involving concerted redistribution of electrons around a six-membered ring; the transfer of the hydrogen atom appears to occur before the loss of the olefin molecule. In addition, it is misleading to visualize the transferred hydrogen as a proton, neutral atom, or hydride ion. The driving force for the rearrangement is the lowering of the activation energy made possible by a three-center bond in the transition state. Removal of an electron from oxygen by ionization provides the driving force, because electron removal results in one instead of two electrons in an antibonding orbital of the three-center bond. In reality, the absence of an electron, not the presence of an unpaired electron, lowers the energy of the three-center system; with no electrons in the antibonding orbital, the bond would be similar to the stable bond found in the boron hydrides.[38] An unpaired electron does not accompany the transferring hydrogen (Table Ia), which has a high net positive charge in the transition state (Table Ib). The reaction can take place with little change in the relative positions of the three atoms: the hydrogen bonded first to the γ-carbon by a σ bond, then bonded to both the carbon and the oxygen with a three-center bond, and finally to the oxygen by a σ bond, while the unpaired electron is transferred directly from oxygen to the γ-carbon. A possible representation with arrows is



This notation does not of course imply that we can distinguish individual electrons, but does represent the flow of radical density in the transition state. However, since the main use of such arrows is for electron bookkeeping, a representation of the type shown previously in reaction 2 adequately denotes the over-all course of the reaction.

Appendix. Estimation of Ion Energies from MO Calculations

Some attention should be given to the problem of obtaining the energies of positive ions formed by the loss of an electron from a neutral molecule. To put the discussion in perspective, some review of differing methods for obtaining the energies of neutral species will be useful. The Hartree–Fock closed-shell molecular energy may be written as

$$E^0 = \sum_{i=1}^{n} E_i^m + \sum_{i=1}^{n} \epsilon_i^m + N \tag{6}$$

where the E_i^m are the molecular one-electron (kinetic plus nuclear attraction) energies in the *i*th MO, the ϵ_i^m are the eigenvalues of the one-electron Hamiltonian, and N is the classical sum of nuclear–nuclear repulsions. The superscript m has been introduced to distinguish molecular from atomic (a) terms, while n represents the number of electron pairs in the neutral molecule. Using the relation

$$\epsilon_i^m = E_i^m + \sum_j (2J_{ij} - K_{ij}) \tag{7}$$

where $\Sigma_j(2J_{ij} - K_{ij})$ are the two-electron terms, we can rewrite (6) as

$$E^{0\prime} = 2\sum_i \epsilon_i^m - \sum_{i,j} (2J_{ij} - K_{ij}) + N \tag{8}$$

The frequent, and generally successful,[39] practice of equating the molecular energy to the sum of molecular eigenvalues has in the past been justified by the assumption[40] that the second and third terms of (8), that is, the electron–electron and nuclear–nuclear repulsions, approximately cancel one another. This assumption is, of course, expected to break down for positive ions formed by loss of an electron from neutral species, since the ions will have fewer electronic repulsions.[41] For this reason, the validity of ion energetics as calculated from sums of eigenvalues has been questioned, particularly where substantial variations in internuclear distances are involved.

In the LCAO–SCF method the terms of eq 8 are evaluated exactly, and many such calculations are now available. These results show that cancellation of the

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(36) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, 71, 2903 (1967).

(37) (a) F. W. McLafferty and W. T. Pike, *J. Am. Chem. Soc.*, 89, 5953 (1967); (b) T. W. Shannon and F. W. McLafferty, *ibid.*, 88, 5021 (1966).

(38) A number of cases have been cited [G. Spiteller, M. Spiteller-Friedmann, and R. Houriet, *Monatsh. Chem.*, 97, 121, (1966)] in which such a rearrangement apparently occurs in an even-electron ion. The general mechanism presented here could still be applicable to these cases if structural effects can appreciably reduce the electron density in the rearrangement region of the antibonding MO of the transition state. We note, however, that electronic excitation analogous to the n,π* state of the Norrish II reaction is an alternative explanation.

(39) (a) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, 37, 2872 (1962); (b) R. Hoffmann, *ibid.*, 39, 1397 (1963).

(40) J. C. Slater, "Structure of Molecules and Solids," Vol. I, McGraw-Hill Book Co., Inc., New York, N. Y., 1963, p 106.

(41) R. Hoffmann, *J. Chem. Phys.*, 40, 2480 (1964).

second and third terms of (8) does not occur;[11] in many cases the electron–electron term is several times larger than the nuclear repulsion. Nevertheless, an alternate approximation[11-15] can be invoked to maintain the use of molecular eigenvalues to give the molecular energy. Instead of eq 6 we write

$$E^0 = \sum_{i=1}^{n} \epsilon_i{}^m + \sum_{i=1}^{n} E_i{}^a \qquad (9)$$

where the $E_i{}^a$ are the one-electron energies of filled atomic orbitals of the constituent isolated atoms, and therefore do not depend on molecular geometry. The approximation underlying (7) is a cancellation of the differences of the atomic and molecular one-electron energies against the nuclear repulsions. While this

$$N - \left(\sum_{i=1}^{n} E_i{}^a - \sum_{i=1}^{n} E_i{}^m\right) = 0 \qquad (10)$$

cancellation is not exact, the sum of the terms on the left side of (10) has been shown in all cases studied to be a very small number compared to the terms themselves.

Equation 9 is very useful because our method of approximating the SCF Hamiltonian gives values of $\epsilon_i{}^m$ in good agreement with SCF results,[12] but does not evaluate the $E_i{}^m$. Values of E^0 obtained in this way are sufficiently accurate to give binding energies of the right order of magnitude; in fact, these energies are not markedly less reliable than those from the SCF functions on which the calculations are based. We note here that the sum of eigenvalues in (9) differs by a factor of 2 from that in (8). For closed-shell species these alternate methods of evaluation give relative energies that differ only by the same factor of 2. When we consider ionic or excited species, however, we will see that (8) and (9) can give dramatically different results.

While we cannot expect to apply eq 9 directly to positively charged species, a way out of our difficulty is suggested by the observation[42,43] that the energy of the highest filled molecular orbital is a good approximation to the vertical ionization potential, *i.e.*, IP $= -\epsilon_n{}^m$. Hence, we may write the ionic energy E^+ as

$$E^+ = E^0 - \epsilon_n{}^m \qquad (11)$$

A similar relationship may be written for the energy E^* of the excited state of the neutral molecule[44]

$$E^* = E^0 - (\epsilon_n{}^m - \epsilon_{n+1}{}^m) \qquad (12)$$

where $\epsilon_{n+1}{}^m$ signifies the energy of the lowest vacant molecular orbital.

We have already seen that eq 11 and 12 give very reasonable over-all energetics for the γ-hydrogen rearrangements of 2-pentanone. On the other hand, the energy barrier calculated from (9) would be prohibitively high because of the large rise in energy of $\epsilon_n{}^m$ in the transition state. However, the conclusion that the ionic or excited-state energies are independent of the energy of the singly occupied MO, $\epsilon_n{}^m$, apparently contradicts our earlier observation based on the simple Hückel approach that the energy barrier is related to the antibonding character of ψ_2 in the C–H–X system. This line of reasoning would ascribe the calculated barrier instead to the energies of the remaining MO's 1–23, which would include the contribution of the symmetric three-center-bonded Hückel MO ψ_1. This apparent contradiction arises from neglect of the one-electron energies and the nuclear repulsions, and can be resolved if care is taken to partition the energy terms correctly. One approach to such partitioning is to assume that the ionic energy can be obtained from eq 6 by giving half-weight to the highest filled MO (eq 13). For the γ-hydrogen rearrangements under consideration, the second bracketed term represents the energy contribution from the highest filled (or nonbonded) MO, while the effect of the three-centered C–H–X bonding orbital will be included in the first bracketed term. Combining (6), (11), and (13) we readily obtain

$$E^+ = \left[\sum_{i=1}^{n-1} \epsilon_i{}^m + \sum_{i=1}^{n-1} E_i{}^m + N\right] + [0.5E_n{}^m + 0.5\epsilon_n{}^m] \qquad (13)$$

$$E_n{}^m = \epsilon_n{}^m \qquad (14)$$

Using (10), we may then rewrite (13) as

$$E^+ = \left[\sum_{i=1}^{n-1} \epsilon_i{}^m + \sum_{i=1}^{n} E_i{}^a - \epsilon_n{}^m\right] + \epsilon_n{}^m \qquad (15)$$

where the effects of the bonded and nonbonded C–H–X orbitals are now isolated in the bracketed term (defined as $E^+{}_{\text{core}}$) and in $\epsilon_n{}^m$, respectively. The argument for the excited state is similar.

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[42] T. Koopmans, *Physica*, **1**, 104 (1934).

[43] R. S. Mulliken, *J. Chem. Phys.*, 46, 497, 675 (1949).

[44] Equation 7, when used with SCF–LCAO or simulated SCF–LCAO wave functions, usually predicts that less energy is needed to ionize the molecule than to effect the n,π^* transition. This embarrassing result is caused by the lack of physical reality of the unoccupied, or "ghost," MO's obtained from these calculations. A rigorous calculation for an n,π^* state could give a more realistic energy, but is impractical. However, because of the orthogonality of the π^* orbital to the reaction plane, the relative energies should not be seriously affected by this situation.