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A MINDO/3 Study of the Norrish Type II Reaction of Butanal

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Abstract: The MINDO/3 semiempirical SCF MO method, although parametrized to fit ground-state (S_0) energies and geometries of molecules, has been found to give useful estimates of the energies of the lowest singlet (S_1) and triplet (T_1) excited states. It has accordingly been used to study the Norrish type II reactions of butanal, by calculating relevant parts of the S_0, S_1, and T_1 potential surfaces. The triplet reaction is predicted to take place via a stable biradical intermediate. The singlet reaction can, however, by-pass the biradical by a mechanism involving direct conversion to the product, via a narrowly avoided S_0–S_1 crossing. These conclusions are in agreement with the results of published photochemical and pyrolytic studies.

Introduction

Work in these laboratories[2] over the last 13 years led to the development of a semiempirical SCF MO treatment (MINDO/3[3]) which has proved remarkably effective in the study of organic reaction mechanisms.[4] While MINDO/3 was parametrized solely to fit experimental heats of formation and geometries of molecules, it has been found to reproduce a very wide variety of other ground-state properties (dipole moments,[3] molecular polarizabilities[4] and hyperpolarizabilities,[5] first ionization potentials,[3] ESCA chemical shifts,[6] molecular vibration frequencies[7] and isotopic shifts,[8] entropies[9] and specific heats,[9] kinetic isotope effects,[8,9] nuclear quadrupole coupling constants,[10] NMR[11] and ESR[12] parameters, and the electronic band structure of polymers[13]). This versatility is rather remarkable, because most of these properties are unrelated to the ones used in the parametrization.

MINDO/3 also reproduces the relative energies of the lowest singlet and triplet states both of methylene[14,15] and of the oxygen molecule (O_2)[15] satisfactorily, the results being indeed as good as, or better than, those given by rather sophisticated ab initio procedures. While these molecules both have triplet ground states, the success of MINDO/3 in this connection suggested that it might be equally effective in predicting the energies of the lowest triplet excited (T_1) states of normal closed-shell molecules and extensive tests have shown that this is indeed the case.[16]

These calculations involved use of the "half-electron" (h-e) method,[17] which indeed had already been shown[18] to reproduce the energies of $\pi \rightarrow \pi^*$ triplets for a variety of conjugated hydrocarbons, using the π SCF MO treatment developed in these laboratories.[19] The latter calculations also led to reasonable estimates of the energies of the lowest $\pi \rightarrow \pi^*$ singlet excited states (S_1) of the molecules in question, using a simple extension of the h-e treatment of triplets.

In view of this, it seemed likely that MINDO/3 should be able to provide useful estimates of the energies of singlet excited (S_1) states in general and so prove useful in the study of photochemical reactions. Such an extension could prove extremely useful because the mechanisms of photochemical reactions are much less well understood than those involving ground-state species and because MINDO/3 has proved of

major value in the latter area. Moreover, studies of several chemiluminescent reactions have already led to novel and important conclusions.[20] When, however, we began to study S_1 energies in a systematic way, we found that the methods used previously to estimate them by the h-e approximation were in error. Here we describe a rigorous procedure for the purpose and results for a number of molecules.

Since this approach seemed encouraging, we decided to apply it to a standard photochemical reaction. We chose the Norrish type II reaction, for three reasons. First, it is one of the best known and most investigated photochemical processes.[21-24] Second, in spite of all this study, its mechanism is still not fully established. Third, as far as we know, no quantitative theoretical study of the Norrish type II reaction has as yet been carried out.[25] This is not in fact surprising, because even the simplest such reaction, i.e., that of butanal (**1**), involves a system with 13 atoms (and hence 33 degrees of freedom) and 28 valence electrons. The calculations must, moreover, be carried out for three distinct potential surfaces, the two lowest singlets (S_0, S_1) and the lowest triplet (T_1). An adequate study by the Roothaan–Hall (RH; "ab initio SCF") method would be out of the question, even if a minimum basis set were used (when the results would in any case be quite unreliable). This indeed is quite a formidable problem even for MINDO/3, because the necessary geometry optimizations are much slower for open-shell systems than for closed-shell ones (vide infra). Since our primary purpose was in any case to explore the applicability of MINDO/3 in this kind of connection, we therefore confined our study to the most salient features of the reaction, seeking in particular to establish whether or not a biradical intermediate is involved and the differences, if any, between the mechanisms of reactions involving the S_1 and T_1 surfaces.

Method

The calculations were based upon the half-electron[17] (h-e) method, modified by inclusion of configuration interaction (CI). In the h-e method, the standard closed-shell SCF procedure for ground states is adapted for calculating open-shell excited singlet or triplet states.

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The Fock matrix used in the h-e method is as follows:

$$F_{pq} = H_{pq} + \sum_i^{occ} \frac{1}{2} n_i [2(ii/pq) - (iq/pi)] \qquad (1)$$

Here $H_{pq} = \int \psi_p H \psi_q d\tau$, $(ab/cd) = \int \psi_a(1)\psi_b(1)1/r_{12}$. $\psi_c(2)\psi_d(2)d\tau_1 d\tau_2$, ψ_i is an MO, H is the MINDO/3 core Hamiltonian, and n_i is the occupation number of ψ_i. This is a quasi-closed shell Fock matrix, since the only difference between closed and open shells lies in the occupation numbers of the MOs. For closed shells all MOs are doubly occupied, whereas for open-shell singlets and triplets the highest two MOs are singly occupied. For closed-shell ground states, eq 1 gives exactly the Fock matrix which results from application of the variational theorem to the ground-state energy. For open shells this is not true, and one must apply a correction to the energy calculated via eq 1. Thus, the h-e correction to the energy of an open-shell singlet is[18] $-\frac{1}{4}(J_{kk} + J_{ll}) + \frac{3}{2}K_{kl}$ and that for a triplet[18] is $-\frac{1}{4}(J_{kk} + J_{ll}) - \frac{1}{2}K_{kl}$, the difference being $2K_{kl}$. Note that in this approximation the MOs of the singlet and triplet are identical, being eigenvectors of the same Fock matrix.

Jungen[26] has shown that in general CI is necessary to describe both singlet and triplet open-shell systems calculated via eq 1. This idea has been explored independently by Salem and co-workers[27] and applied to the case of biradicals. They showed that three configurations are important in describing biradicals; the parent, or h-e, configuration in which the $2k$ electrons in the molecule are distributed over the MOs ψ_i with an orbital occupancy of $\psi_1^2\psi_2^2 \ldots \psi_{k-1}^2\psi_k\psi_{k+1}$, and two closed-shell configurations $\psi_1^2 \ldots \psi_{k-1}^2\psi_k^2$ and $\psi_1^2 \ldots \psi_{k-1}^2\psi_{k+1}^2$, the former being what one normally thinks of as the "ground state" of the system. In the case of biradicals, however, the ground state is well represented by the h-e configuration alone if ψ_k and ψ_{k+1} are localized on separate radical centers, since the h-e configuration then corresponds to a covalent state. The closed-shell configurations are then ionic and are associated with excited states of the biradical. For ordinary molecules close to their equilibrium geometries (no severely stretched bonds), the h-e configuration is associated with the lowest excited state, and the first of the above two closed shell configurations corresponds to the ground state.[28]

Our early experience has shown the (3×3) CI described above to be adequate for the description of biradicals, but inadequate for the complete description of reactions involving carbonyl groups. Our CI method, therefore, allows the inclusion of all single and double excitations with respect to the formal "ground state" configuration $\psi_1^2 \ldots \psi_{k-1}^2\psi_k^2$. In this scheme, the h-e configuration is a singlet or triplet eigenstate of S^2 consisting of the proper linear combination of Slater determinants.

Prior to the search for a particular stationary point on a given potential surface, configurations were chosen as follows. In the systems studied it was always possible to pick the three or four major configurations by inspection. With the molecular geometry in the neighborhood of the stationary point, these were then included in a series of CI calculations in which both single and double excitations were systematically examined. Several calculations were required because the CI matrix was dimensioned to (52×52). As many as 500–800 configurations were examined in this way. Those configurations having a coefficient in the CI expansion numerically larger than 0.04 were retained in the subsequent search for the stationary point. Usually a total of between 10 and 20 configurations were selected by this procedure.

Geometries were as usual calculated by minimizing the energy with respect to all coordinates other than those being used to follow reactions. The geometry optimizations were carried out by a modification of the standard[3] Davidon-Fletcher-Powell[29] (DFP) method. In closed-shell molecules, the necessary derivatives of the energy can be found very rapidly in MINDO/3 either analytically[30] or by finite difference because the bond order matrix is variationally optimized and so first order invariant for changes in the integrals. In calculating derivatives of the energy by finite difference, one can therefore evaluate the perturbed energies directly from the expression for the total energy, using modified values for the integrals. The time required for this is almost negligible. The same would be true in a multiconfiguration SCF treatment, or a complete CI treatment, but not in one using partial CI, as here. In this case the bond order matrix is no longer first order invariant so derivatives of the energy have to be found by finite difference, using complete SCF calculations at each point. While the resulting procedure is still much faster than non-derivative-optimization procedures such as Simplex, the time required is also very much greater than that for an analogous closed-shell molecule.

Transition states were located approximately by using an appropriate internuclear distance (r) as a reaction coordinate and minimizing the energy with respect to all other geometrical variables for various values of r ranging from that in the reactants to that in the product. The maximum in a plot of energy vs. r gave an approximate structure for the transition state and this was then refined by minimizing the scalar gradient (see McIver and Komornicki[30]), using an optimization procedure due to Dr. Bartels and a program by Dr. P. K. Weiner.

Results

First we studied butanal (**1**). The calculated heats of formation and equilibrium geometries of the ground state (S_0), and of the lowest excited singlet (S_1) and triplet (T_1) states, are shown in Figure 1. The main differences between the S_0 state and the S_1 and T_1 states are a lengthening of the C_1O bond (see **1**) and the pyramidal geometry of C_1 in S_1 and T_1.[31] Including additional configurations in the CI treatment had virtually no effect on the energies of any of these states.

The Norrish type II reaction of **1** was studied using the H_8O distance (see **1**) as the reaction coordinate, the calculations being carried out initially with a (9×9) CI treatment for both S_1 and T_1. These included the two closed-shell configurations mentioned above *plus* others involving the n, π, and π^* orbitals. Problems arose in refining[30] the transition states located in this way since both the S_1 and T_1 surfaces are almost flat in the vicinity of the saddle points. The resulting numerical instabilities caused the minimization routine to stop when the gradient components were merely very low rather than sensibly zero.[32] The transition states thus calculated have the geometries shown in Figure 2 and heats of formation of 23.84 ((9×9) CI) and 19.74 kcal/mol ((7×7) CI) for S_1 and T_1, respectively. This gives values of $\Delta H^{\ddagger}$ of 9.14 and 11.74 kcal/mol for γ-hydrogen abstraction on the S_1 and T_1 surfaces, respectively. The various stationary points are indicated schematically in Figure 3.

A local minimum was found on the S_0 surface, corresponding to a 1,4 biradical (**2**) in which carbons C_1 and C_4 are in a gauche relationship (Figure 4). At this geometry, the energies of S_0 (three configurations) and T_1 (one configuration) are -8.11 and -7.83 kcal/mol, respectively.[33] It was found that γ-hydrogen transfer on the T_1 surface of butanal results in a smooth decrease in energy from the transition state to this biradical geometry. The near degeneracy of S_0 and T_1 thus allows efficient intersystem crossing, providing that spin–orbit matrix elements are large enough.

Back-transfer of hydrogen from the biradical to form butanal on the S_0 surface was examined from a plot of energy vs. OH_8 distance, all other geometrical variables being optimized. The energy profile for this process suggests that the transition
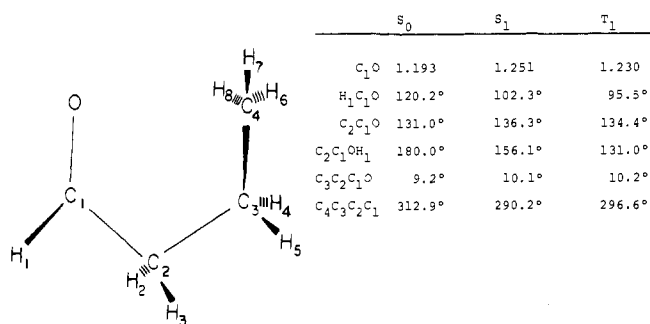
	S_0	S_1	T_1
C_1O	1.193	1.251	1.230
H_1C_1O	120.2°	102.3°	95.5°
C_2C_1O	131.0°	136.3°	134.4°
$C_2C_1OH_1$	180.0°	156.1°	131.0°
$C_3C_2C_1O$	9.2°	10.1°	10.2°
$C_4C_3C_2C_1$	312.9°	290.2°	296.6°

Figure 1. Calculated geometries (bond lengths in Å) and heats of formation (ΔH_f, kcal/mol at 25 °C) for butanal: (a) S_0 state; (b) S_1 state; (c) T_1 state. The dihedral angle $\angle abcd$ is the rotation of ab relative to cd, measured clockwise in the direction $b \rightarrow c$.

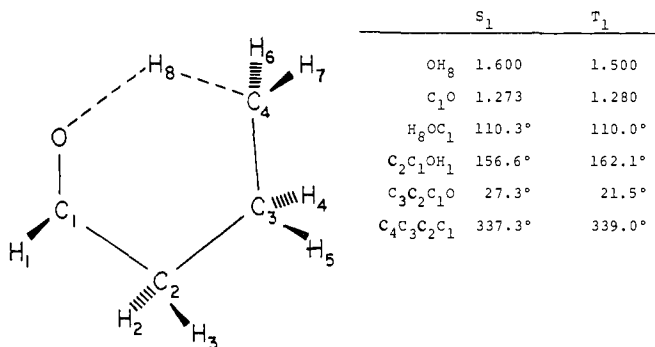|	S_1	T_1
OH_8	1.600	1.500
C_1O	1.273	1.280
H_8OC_1	110.3°	110.0°
$C_2C_1OH_1$	156.6°	162.1°
$C_3C_2C_1O$	27.3°	21.5°
$C_4C_3C_2C_1$	337.3°	339.0°

Figure 2. Calculated geometries of the transition states for internal hydrogen transfer in the singlet and triplet Norrish type II reaction of butanal: (a) singlet; (b) triplet.

state occurs at about $OH_8 = 1.08$ Å with a heat of formation of not greater than -2.0 kcal/mol, giving $\Delta H^{\ddagger} \approx 6$ kcal/mol for back-transfer of hydrogen.

In contrast to the T_1 surface, the S_1 energy (see Figure 3) decreases with decreasing OH_8 distance from the transition state to a local minimum at 9.674 kcal/mol, with $OH_8 = 1.062$ Å (Figure 5). At this geometry, the S_0 energy is 9.615 kcal/mol, both energies being roots of an (18×18) CI matrix, including 13 single and 4 double excitations. At this same geometry, a (29×29) CI (configurations with S_1 coefficients ≥ 0.03) produced energies of 7.847 and 9.260 kcal/mol for S_0 and S_1. That the intended crossing is so weakly avoided is not surprising, since the arrangement of atoms H_1, C_1, C_2, C_4, O, H_8 is not far from coplanar.[27a]

Starting from the local minimum on the S_0 surface at -8.11 kcal/mol, corresponding to the biradical, the cleavage to acetaldehyde enol and ethylene was investigated using the C_2C_3 distance (see **1**) as the reaction coordinate and optimizing all other geometrical variables. A search for the transition state at the apex of the resulting energy curve yielded a stationary point at 1.97 kcal/mol (13 configurations) shown in Figure 6, giving $\Delta H^{\ddagger} = 10.1$ kcal/mol for cleavage of the biradical.[32]

Closure of the biradical (**2**) to cyclobutanol (**3**) was investigated by studing the reverse reaction, the opening of **3** to **2**. Using the C_2C_4 distance (see **3**) as the reaction coordinate and optimizing all other geometrical variables, we found that the energy of S_0 increased as the C_2C_4 bond (see **3**) of cyclobutanol was stretched up to 2.5 Å (-4.9 kcal/mol), with the terminal CH_2 and CHOH groups always face to face. The local biradical minimum at -8.1 kcal/mol has a skew relationship between the terminal groups rather than face to face (see Figure 4), implying that the transition state for closure (which was not sought in this study) involves merely a mutual rotation of the terminal groups into a face to face conformation, followed by a monotonic decrease in energy.
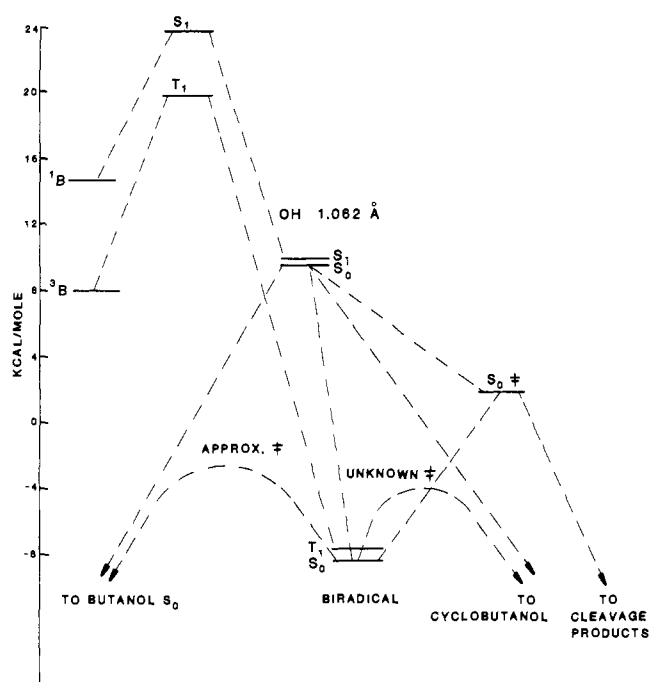

Figure 3. Schematic representation of the calculated energies of stationary points in the Norrish type II reactions of butanal.
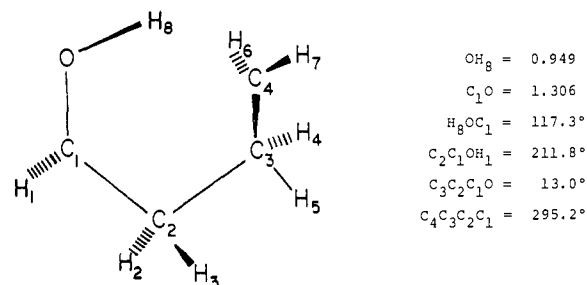

OH_8	=	0.949
C_1O	=	1.306
H_8OC_1	=	117.3°
$C_2C_1OH_1$	=	211.8°
$C_3C_2C_1O$	=	13.0°
$C_4C_3C_2C_1$	=	295.2°

Figure 4. Calculated geometry for the S_0 biradical **2** ($\Delta H_f = -8.11$ kcal/mol).

Considerable attention was devoted to deactivation from S_1 to S_0 in the region of the weakly avoided S_1–S_0 crossing. In the absence of any information on Franck–Condon factors, we assumed that vertical deactivation from S_1 to S_0 is favored in this region. The procedure was to find paths of monotonically decreasing energy on S_0, starting from geometries previously calculated in the avoided-crossing region of the S_1 surface. Thus, the points previously calculated on the S_1 surface, having $OH_8 = 1.20, 1.15, 1.10, 1.062$, and 1.00 Å, were optimized on the S_0 surface (nine configurations) with no geometrical constraints. In each case, the molecule reverted to butanal with retention of stereochemistry at carbon C_4.

Deactivation on S_0 from the geometry of the S_1 local minimum at $OH_8 = 1.062$ Å to the cleavage products was examined by varying both the OH_8 and C_2C_3 distances while optimizing all other geometrical variables, beginning with the geometry of the S_1 local minimum and ending with the geometry of the transition state for cleavage from the biradical. Twenty-four configurations were chosen from those used to describe the S_1 local minimum ($OH_8 = 1.062$ Å) and the cleavage transition state. The path was as follows: $OH_8 = 1.05$ Å, $C_2C_3 = 1.70$ Å, $E = 8.16$ kcal/mol; OH = 1.05 Å, CC = 1.80 Å, $E = 7.74$ kcal/mol; OH = 1.00 Å, CC = 1.90 Å, $E = 5.08$ kcal/mol; OH = 0.95 Å, CC = 1.96 Å, $E = 2.51$ kcal/mol. This last point had a geometry very close to that of the cleavage transition state, and from here the energy can continue to decrease to the cleavage products. This path is stereospecific, in that stereo-
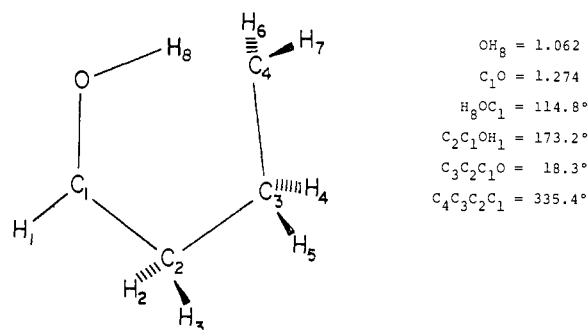
$$OH_8 = 1.062$$
$$C_1O = 1.274$$
$$H_8OC_1 = 114.8°$$
$$C_2C_1OH_1 = 173.2°$$
$$C_3C_2C_1O = 18.3°$$
$$C_4C_3C_2C_1 = 335.4°$$

Figure 5. Calculated geometry for the local minimum on the S_1 surface ($\Delta H_f = 9.674$ kcal/mol).

$$C_1C_2 = 1.383$$
$$C_2C_3 = 1.979$$
$$C_3C_4 = 1.362$$

Figure 6. Calculated geometry of the transition state for $2 \rightarrow (H_2C{=}CH_2 + H_2C{=}CHOH)$.

chemical relationships originally present in butanal are maintained in the cleavage products.

Deactivation on S_0 from the geometry of the S_1 local minimum ($OH_8 = 1.063$ Å) to cyclobutanol was examined by calculating a 12-point reaction path in which all geometrical variables were varied linearly in 12 increments, starting from the geometry of the S_1 local minimum and ending with a biradical geometry in which $C_1C_4 = 2.3$ Å and the terminal CH_2 and $CHOH$ groups are face to face. This biradical geometry collapses to cyclobutanol when optimized with no geometrical constraints. Using the 18 configurations appropriate to the S_1 local minimum at $OH_8 = 1.062$ Å, the reaction path obtained by this procedure was found to decrease monotonically in energy, with minor adjustments in the geometry of one point. Again, the reaction path was stereospecific in the sense noted above.

A similar 12-point reaction path on the S_0 surface was calculated between the geometry of the S_1 local minimum ($OH_8 = 1.062$ Å) and the biradical local minimum at -8.1 kcal/mol, using the 18 configurations appropriate to the S_1 minimum. Again, a stereospecific reaction path was calculated in which the energy decreased monotonically. An analogous 12-point path in which the change in geometry also involved rotation of the terminal CH_2 by 180° gave a nonmonotonic decrease in energy. The energy first decreased from 9.615 to 6.510 kcal/mol, increased to 7.725 kcal/mol, and decreased monotonically from there. The question was not pursued, but it seems likely that a monotonically decreasing path exists.

Discussion

The mechanism for the Norrish type II reaction of butanal implied by these studies is summarized in Scheme I. The triplet aldehyde (^3B) undergoes γ-hydrogen abstraction with $\Delta H^{\ddagger} = 11.74$ kcal/mol, followed by deactivation to the biradical (^3BR), crossing to S_0, and subsequent competition among cleavage, closure, and back-transfer to form butanal. The excited singlet aldehyde abstracts hydrogen with $\Delta H^{\ddagger} = 9.14$ kcal/mol and goes to a local S_1 minimum ($^1B'$) looking somewhat like a biradical with a stretched OH bond, and which is very close in energy to S_0. Deactivation to S_0 at this point can lead stereospecifically and without activation to butanal, cyclobutanol, or cleavage products, and nonstereospecifically to the 1,4 biradical ^1BR. The prediction of product ratios resulting from reaction in the singlet manifold is impossible from a consideration of potential surfaces alone, being controlled entirely by the dynamics of the reaction.

The adiabatic excitation energies calculated in this study are 70.6 kcal/mol for the S_0-S_1 splitting and 63.9 kcal/mol for the S_0/T_1 splitting, compared with experimental values of 85[34] and $\sim$78[35] kcal/mol, respectively. It is interesting that, although the absolute values are low by 14 kcal/mol, the difference in energy between S_1 and T_1 is correctly predicted. This suggests again that the shapes of the calculated potential
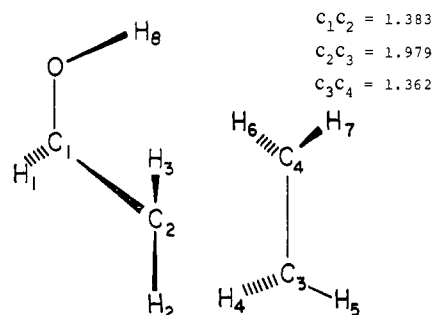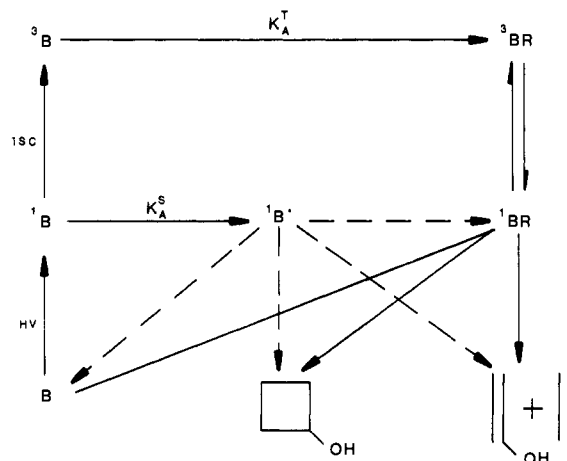
Scheme I

surfaces are reliable, at least in a qualitative sense. In addition, the deviation from planarity about the carbonyl carbon in S_1 and T_1 butanal follows the same trend as in formaldehyde.[36] Both are significantly pyramidal, but the T_1 state is more so.

The triplet lifetime of butanal in benzene at 30 °C was reported by Coyle to be 3.5×10^{-8} s.[37] Assuming by analogy with alkanones[38] that radiationless deactivation from the triplet is much slower than hydrogen abstraction, one obtains (cf. Scheme I) $k_a^T = 2.9 \times 10^7$ s^{-1}. Recent data of Dalton et al.[39] suggest that in hexane solution $k_a^S = 1.6 \times 10^8$ s^{-1} for butanal, although their quoted experimental error is as large as the value itself. A less uncertain value exists for 2-pentanone[40a] in hexane, for which $k_a^T = 1.3 \times 10^7$ s^{-1} and $k_a^S = 1.8 \times 10^8$ s^{-1}. Taking $\log A = 12$,[25] the results for butanal imply that $E_a(S_1) = 5.2$ and $E_a(T_1) = 6.3$ kcal/mol, and for 2-pentanone $E_a(S_1) = 5.2$ and $E_a(T_1) = 6.8$ kcal/mol. Similar values have been found for the reactions of alkyl phenyl ketones,[41] and for 2-pentanone in the gas phase.[40b,c]

Our calculated $\Delta H^{\ddagger}$ values are too high by about 4–5 kcal/mol,[40,41] about the limit of reliability for absolute heats of formation for most ground-state MINDO/3 calculations.[3] The situation is much better with regard to relative rates. In agreement with experiment, MINDO/3 predicts a faster hydrogen abstraction on the S_1 surface, giving $\Delta\Delta H^{\ddagger} = 2.6$ kcal/mol, compared with $\Delta\Delta H^{\ddagger} \approx 1.1$ kcal/mol for butanal and 1.6 kcal/mol for 2-pentanone.

No direct measurement has yet been made of the rate constant for cleavage of a 1,4 biradical. However, Wagner[42] has used an intramolecular trapping experiment to estimate the lifetime of the biradical generated from triplet α-allylbutyrophenone to be about 10^{-6} s. Provided that only singlet biradicals were being trapped in this experiment,[43] the maximum rate constant for cleavage of the biradical[44] is 6×10^5

Table I. Product Ratios in Photochemical Reactions of Ketones and Related Thermolysis

compd	solvent	temp, °C	% ketone[a]	% cyclization[a]	% cleavage[a]	ref
T: (structure)	hexane	amb	57	12	31	3b,c
S: (structure)	hexane	amb	90	0.7	8.2	3b,c
T: (structure)	hexane	amb	19	24	57	1, 3c
S₁ (structure)	hexane	amb	86	0.09	13	3a,c
(structure) OH	gas phase	381	6	23[b]	71	30
OH (structure)	gas phase	312	~10		~90	31

[a] For photochemical reactions, these values are taken from quantum yields observed for the appropriate spin multiplicity. The amount of ketone (radiationless decay) from S_1 reactions is taken as $1 - \Phi(\text{isc}) - \Phi_S(\text{clv}) - \Phi_S(\text{cyc})$. The amount of ketone from T_1 reactions is taken as $\Phi(\text{isc}) - \Phi_T(\text{clv}) - \Phi_T(\text{cyc})$. For thermal reactions, these values are product ratios resulting from the appropriate biradical. [b] We assume that the total amount of cyclization is about twice the amount of *trans*-1,2-dimethylcyclobutanol formed.

s^{-1}. With $\log A = 12$, this gives $E_a = 8.6$ kcal/mol for cleavage of the biradical, compared to our calculated value of 10.1 kcal/mol. Although the measurement was made on a phenyl-substituted biradical, the closeness of the two values is encouraging. In these calculations we chose to examine only the cleavage of the "syn" biradical rather than the "anti" biradical. Although the latter might be important in determining product ratios from decay of the biradical itself, it is not a necessary feature of our proposed mechanism of singlet type II reactions.

The prediction that the triplet reaction proceeds solely through the biradical comes as no surprise. Abundant evidence has accumulated which implicates the biradical as an intermediate in type II reactions of n → π* triplets.[21-23,25] Of greater interest is the prediction that a weakly avoided S_1-S_0 crossing exists in the hydrogen transfer path.[45] The local minimum in S_1 along this path could have been predicted from qualitative arguments, as Salem[25b,c,27] has pointed out, since it is easily seen that hydrogen abstraction by the (n → π*) state of a carbonyl group, in which a plane of symmetry is maintained, necessarily involves an intersection of S_0 and S_1. A distortion from C_s symmetry produces the avoided crossing and a local minimum on S_1. An obvious corollary is that in those ketones where steric hindrance disfavors the conformations which approximate a C_s abstraction, the crossing will be much more avoided than in the case of butanal. In perverse cases this local minimum in S_1 might disappear altogether.

The avoided crossing on the hydrogen abstraction pathway offers an efficient means for crossing from S_1 to S_0 at the geometry corresponding to the S_1 local minimum. The assumption of vertical deactivation is probably valid, since the crossing is weakly avoided and therefore almost classically allowed. We have seen that after crossing to S_0, the system must choose among several paths of monotonically decreasing energy: cyclization, cleavage, back-transfer of hydrogen to form butanal, or biradical formation with subsequent competition among the first three modes of reaction. The products may thus be formed directly, without going through a biradical. Product ratios are the result of a purely dynamical competition among the four major modes of deactivation from the avoided crossing region. Any approach to a theoretical understanding of the product ratios in the singlet reaction must take account of the fact that the initial vibrational population distribution of S_0 is highly non-Boltzmann, owing to the nonadiabatic crossing.

Several experiments have been published which oppose an interpretation of singlet type II reactions in which all products and radiationless decay proceed via a biradical intermediate. On the other hand, these experiments are consistent with the notion that products and radiationless decay are formed as in Scheme I.

Wagner[46] and Barltrop and Coyle[47] have measured quantum yields for type II reactions for ketones dissolved in inert hydrocarbon or alcohol, both quenched and unquenched. In the absence of triplet quencher, they found that quantum yields for the type II reaction were dramatically greater in alcohol than in the hydrocarbon solvent, in some cases approaching unity. In the presence of excess triplet quencher, the change of solvents produced no change in quantum yield. In the case of the triplet reaction, the solvent effect has been explained by invoking specific solvation (H bonding) of the hydroxy biradical by the alcohol, which prevents disproportionation of the biradical to form ketone.[48] The fact that this cannot be occurring in the singlet reaction means either that the singlet biradical is too short lived to be solvated or that the singlet reaction proceeds to an unmeasurably small extent via a biradical. The first possibility is rendered very unlikely by the experiments of Casey and Boggs,[23] who observed a 5–10% loss of stereochemistry in the 2-butenes resulting from the singlet type II reaction of *threo*- and *erythro*-4-methyl-2-hexanone-5-d_1. In this reaction some singlet biradicals are probably formed, which live long enough to allow C–C bond rotation. Since it is inconceivable that hindered C–C bond rotation is faster than solvation, we prefer to believe that most singlet type II reactions involve biradicals only to a small extent. The lack of a solvent effect is precisely what one would expect from the mechanism in Scheme I. The lifetime of $^1B'$ might indeed be shorter than the rotational correlation time of *t*-BuOH or MeOH, thus preventing solvation. Even if solvation did occur, we predict a large monotonic decrease in energy from $^1B'$ to B, certainly more than enough to break a hydrogen bond.

Table I presents the results of both photochemical and thermal reactions thought to involve biradical intermediates. Internal comparisons between S_1 and T_1 states of each ketone show that the product distributions resulting from these states are totally different. A mechanism which requires both S_1 and T_1 reactions to go through biradicals cannot easily account for these results, because all the products would then be formed on the S_0 surface. If the S_1 reaction were to go solely through a biradical, one would have to assume that this singlet biradical is fundamentally different from the singlet biradical formed

by crossover from the triplet biradical involved in the T_1 reaction. Although there is evidence that this may be the case for certain biradicals, it seems much more likely that here biradicals are not in fact involved in the S_1 reaction.

Further evidence for this conclusion comes from studies[49,50] of pyrolytic reactions in which singlet biradicals are formed by alternative paths, on the S_0 surface. The results are summarized in Table I. Let us assume that the three products listed arise both in the photochemical (S_1) reaction and in the thermal reaction via the same singlet biradicals. The ratios of the Arrhenius preexponential factors for formation of ketone (A_{ket}), cyclization (A_{cyc}), and fission (A_{fis}) are expected[24,51] to be in the ratio $A_{ket}:A_{cyc}:A_{fis} = 0.1:1.0:1.0$. Using the results for the thermal reactions in Table I, we then obtain a value of 1.5 kcal/mol at 381 °C for the difference between the activation energies for cyclization ($E^{\ddagger}_{cyc}$) and fission ($E^{\ddagger}_{fis}$). This agrees well with the value (1.5 kcal/mol) estimated from the photochemical results at 25 °C. However, we also find for the corresponding differences in activation energy for cyclization and ketone formation ($E^{\ddagger}_{ket}$)

$$E^{\ddagger}_{cyc} - E^{\ddagger}_{ket} = 1.2 \text{ kcal/mol at } 381 \text{ °C} \qquad (2)$$

$$E^{\ddagger}_{cyc} - E^{\ddagger}_{ket} = 5.5 \text{ kcal/mol at } 25 \text{ °C} \qquad (3)$$

This major discrepancy is not surprising since it is obvious from Table I that the photochemical and thermal reactions lead to quite different product ratios. It could be explained only by the improbable assumption that the potential surface for a nonpolar biradical species can change drastically in shape on passing from the gas phase to an inert nonpolar solvent. Such a change might increase or decrease the rates of the competing reactions to comparable extents but it seems most unlikely that it could lead to large differential changes in rates. The relative rates of disproportionation and recombination of primary alkyl radicals are, for example, almost completely insensitive to a change from gas phase to solution,[52] and the relative rates of radiationless decay vs. type II reaction in the singlet state are also insensitive to changes in solvent from hexane to alcohol.[46,47] For comparison, the pyrolysis studied by Stephenson and Gibson is also included.[50] It too shows a very small amount of ketone formation, in contrast to the photochemical results. Our conclusion from the comparisons in Table I is that either the singlet photochemical reaction forms a very unusual biradical, fundamentally different from that formed in the pyrolyses, or that the reaction mostly by-passes the biradical.

The conceptual framework implied by Scheme I makes the data in Table I much more intelligible. In this mechanism the relative rates of all processes depend upon the vibrational modes of the S_0 surface to which energy is transferred from the S_1 surface. The pyrolytic and singlet photochemical results are expected to be different, since they represent processes governed by Boltzmann statistics and nonadiabatic transitions, respectively. Similarly, the S_1 and T_1 photochemical results should differ, since the T_1 reaction forms a singlet biradical by crossover from a (presumably thermally equilibrated) triplet biradical. Unfortunately, our complete ignorance of the dynamical consequences of our calculated surface prevents us from making even qualitative predictions of product ratios in the S_1 reactions. One is tempted to predict that the major deactivation from $^1B'$ (see Scheme I) is to butanal, since an optimization of $^1B'$ on the S_0 surface with no geometrical constraints gave butanal directly. This, of course, is in accordance with experiment.[21] The result of such an optimization, however, probably tells us less about chemical dynamics than it does about our optimization procedure.

The final question to be asked is whether the singlet type II reaction actually forms a "very unusual biradical" or whether the reaction essentially by-passes the biradical. This question

has been extensively pursued in a different context by Stephenson and Brauman[53] and by Stephenson and Gibson.[50] Based on the much greater stereospecificity in the products resulting from S_1 type II cleavage compared to those from pyrolyses of the corresponding cyclobutanols, they proposed that the S_1 type II reaction forms a vibrationally excited biradical with enough extra energy to undergo cleavage stereospecifically. Adopting the quasi-equilibrium assumptions of transition state theory and RRKM theory,[54] they point out that as the average energy of the system increases well beyond the energy of the transition state, the rate constant must approach the Arrhenius A factor. Given reasonable values for the A factors for cyclization, cleavage, and C–C bond rotation in the biradical, it is clear that the rotational A factor is smaller than those of the other two processes. Therefore at high internal energies, corresponding to the vibrationally excited biradical, one would expect stereospecific product formation. Unfortunately, this argument does not account for the S_1 photochemical product distributions in Table I. Since one expects $A_{ketone}:A_{cyc}:A_{clv}$ to be about $0.1:1.0:1.0$,[24,51] the above argument predicts this to be the approximate product distribution in the S_1 type II reaction. The results are completely at variance with this prediction. The problem seems to lie first with the identification of $^1B'$ in Scheme I as a biradical, and second with the attempt to apply statistical theories to a nonadiabatic crossing. We have shown that deactivation on the S_0 surface from the avoided crossing region proceeds monotonically downward in energy to the biradical, butanal, cyclobutanol, and cleavage products. Thus the S_1–S_0 crossing produces a molecule ($^1B'$) which is no more a vibrationally excited biradical than it is a vibrationally excited butanal, etc. The very assignment of A factors becomes problematical, since the assignment of the geometry of $^1B'$ to a particular S_0 reactant is purely arbitrary. It is interesting that the thermal reactions in Table I, which do proceed via singlet biradicals, come much closer than the S_1 type II reactions to the results predicted by statistical theories. A proper conceptual framework for understanding the photochemical reaction is that of radiationless transition theory[55] or classical trajectories,[56] in which it is recognized that the final product ratios are determined by the preference during S_1–S_0 crossing for certain modes of nuclear motion over others. Since virtually all photochemical reactions involve nonadiabatic transitions between two surfaces, it is probable that most of these reactions must be treated in this way.

Conclusions

The results reported here suggest that MINDO/3 has provided interesting and useful conclusions concerning one of the most intensively studied of known photochemical processes. The predicted mechanisms seem not only to be consistent with the available experimental data but also to provide a very satisfactory interpretation and unification of them.

The MINDO/3 calculations also suggest that the course of these reactions is not determined solely by electronic and energetic factors, as are most ground-state processes, but rather by subtle dynamic considerations which could be studied only by detailed trajectory calculations on the ground-state and excited-state surfaces. If so, such calculations would have to be based on potential surfaces found by some semiempirical treatment such as MINDO/3 because ab initio methods would be quite impracticable for the purpose.

These conclusions imply that attempts to interpret excited-state chemistry in terms of ground-state concepts are incorrect in principle and likely to prove both unsound and actively misleading, particularly in the case of singlet excited states. This is an independent area of chemistry where the rules may bear little relation to those for ground-state processes. If so, the best hope for elucidating them may well lie in theoretical

studies of the kind reported here, given that even this first application of MINDO/3 has proved so encouraging.

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