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Symmetry Analysis of the Potential Energy Surfaces for the Photochemical Decomposition of Formaldehyde*

Vinzenz Bachler and E. Amitai Halevi**

Institut für Strahlenchemie im Max-Planck-Institut für Kohlenforschung, Stiftstraße 34-36, D-4330 Mülheim a.d. Ruhr, Federal Republic of Germany

Orbital Correspondence Analysis in Maximum Symmetry (OCAMS) is applied to the decomposition pathways of formaldehyde to H_2+CO and to $H+HCO$. The symmetry adapted nuclear motions, which are preferentially incorporated in the energetically favoured fragmentation pathways on both the ground and excited state surfaces are singled out. The results of this analysis are in full agreement with those of published potential energy surfaces and consistent with the results of experimental investigations reported in the literature. The nuclear motions favouring the various processes thus appear to be deducible from considerations of orbital symmetry.

Key words: Formaldehyde fragmentation – Orbital symmetry – Potential energy surfaces.

1. Introduction

Gas phase irradiation of formaldehyde in the 355–280 nm region produces formaldehyde in the n-π^* S_1 state, which decomposes preferentially along two pathways [1]

$$H_2CO^* \rightarrow H_2+CO \quad \text{I}$$

$$H_2CO^* \rightarrow H+HCO \quad \text{II}$$

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[**] Permanent address: Department of Chemistry, Technion – Israel Institute of Technology, Haifa.

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It is generally agreed that at longer wavelengths the molecular process I predominates, whereas the radical decomposition is preferred at shorter wavelengths [1, 2]. Process I has been studied extensively by excitation into definite vibronic levels of the S_1 state using tunable lasers [3, 4]. These investigations resulted in efficient procedures for isotope separation [5] and in the conclusion that process I proceeds on the ground state S_0 potential energy surface [3]. The nonradiative transition from S_1 to S_0 is suggested to occur via coupling of a vibronic level of S_1 with excited vibrational levels of S_0 [3, 6], the important promoting modes being the non-totally symmetric in plane and out of plane bending vibrations [4]. The radical process II is of interest as a model of the photochemical α-cleavage, which is important in organic photochemistry [7]. Thus, there are many reasons why a detailed theoretical analysis of the decomposition mechanisms is of interest.

An essential prerequisite of such an investigation is the ability to identify energetically favoured reaction paths on the potential energy surfaces for processes I and II. However, the quantum chemical determination of such paths is generally a complicated search procedure on the 7-dimensional potential energy hypersurface. Therefore, any technique is valuable which selects those nuclear motions which might be energetically favourable. For such purposes Orbital Correspondence Analysis in Maximum Symmetry (OCAMS) has been proposed [8] and successfully applied [8, 9]. This method is distinguished from other correlation diagram techniques in that: (a) The molecular orbitals of the reactant and the products are initially classified in a symmetry point group common to both, which is not assumed to be retained along the actual reaction path [8]. (b) The procedure then selects the symmetry species of the nuclear displacement which reduces the symmetry of the pathway to a subgroup in which all of the occupied orbitals of the reactant correlate with those of the products [8]. Here we apply OCAMS in order to find the energetically favoured decomposition pathways for I and II. Moreover, we illustrate how these pathways are governed by oribital symmetry.

2. The Molecular Decomposition Pathway

2.1. The Ground State Reaction

All molecular orbitals and their energies have been calculated *ab initio* using the STO-3G basis set [10]. This method should be adequate for determining the symmetry properties of the molecular orbitals and their relative ordering by energy. Figure 1 illustrates how the molecular orbitals of formaldehyde change when the molecular process I is simulated while retaining C_{2v} geometry. The reactant is gradually taken into the geometry of the products along a hypothetical reaction coordinate, constructed from an appropriately phased superposition of the a_1 coordinates (see Fig. 2).

Along this least-motion pathway, the molecular orbitals correlate as shown in Fig. 1. All but one of the occupied molecular orbitals of formaldehyde correlate in C_{2v} with orbitals that are occupied in the final products CO and H_2. The exception, the

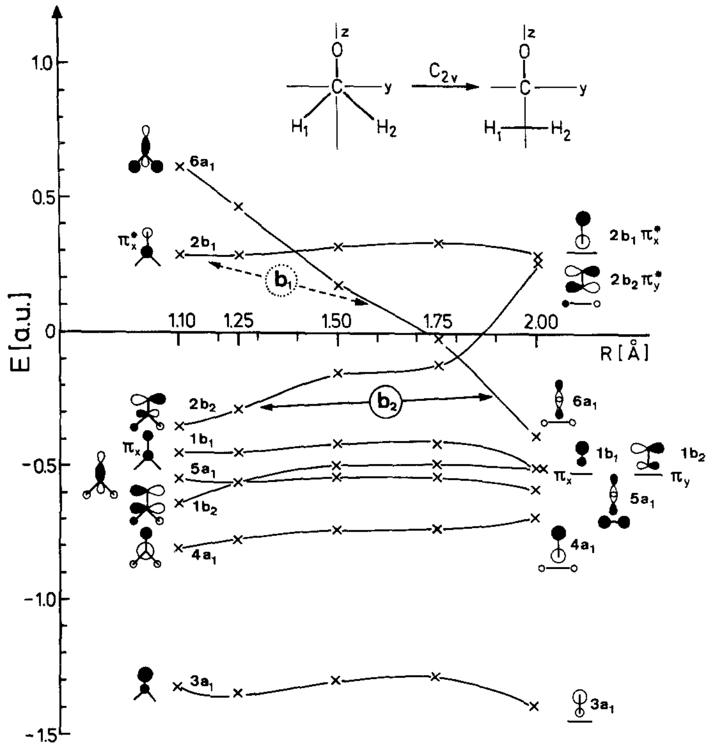

Fig. 1. Molecular orbital changes when the C—H bonds in formaldehyde are elongated, retaining C_{2v} geometry. The equilibrium geometry is taken from Ref. [20]. As the CH distance (R) was increased, the HH distance (r) was decreased as follows (all distances in Å):

$R = 1.25$	1.50	1.75	2.00
$r = 1.50$	1.00	0.75	0.742

The CO-distance was fixed at the experimental value in H_2CO. The omitted inner shell molecular orbitals, $1a_1$ and $2a_1$, correlate directly

lone pair orbital $2b_2$, goes over into the antibonding $2b_2$ orbital localized in the CO nuclear region. Consequently, as long as C_{2v} symmetry is imposed along the pathway, the ground state of formaldehyde correlates with a doubly excited ${}^1A_1$ state of the products, in which two electrons are paired in the $2b_2$ orbital. Therefore, a ground state decomposition pathway in which C_{2v} symmetry is retained is regarded as "forbidden". The decomposition can be made "allowed" by performing a distortion which brings the lone pair orbital $2b_2$ into induced correspondence with the $6a_1$ product orbital [8]. According to OCAMS, a b_2 distortion is required, since the triple direct product $b_2 \times b_2 \times a_1$ yields the totally symmetric representation. OCAMS thus suggests a b_2 distortion, which reduces the symmetry from C_{2v} to C_s, retaining the molecular $\sigma(y, z)$ mirror plane (see Fig. 2). The representations a_1 and b_2 of C_{2v} both map onto a' of $C_s(yz)$.

Ab initio calculations for I have been performed [11] and the OCAMS result is supported by refined calculations for the lowest energy path [12, 13, 14]. Minimal

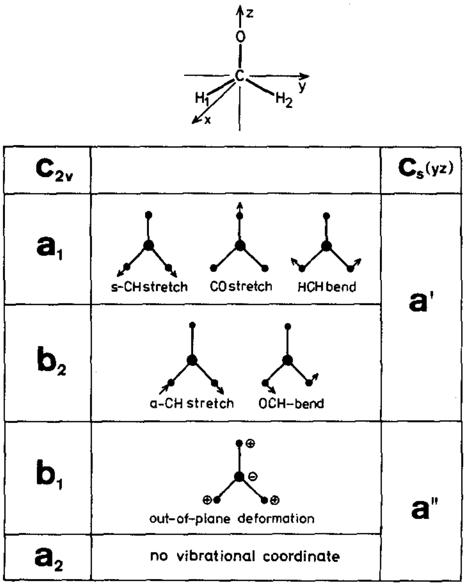

Fig. 2. Axis convention and internal symmetry coordinates of H_2CO

Slater basis set calculations, with extensive CI and a thorough geometry optimization, produce an activation energy of 7.75 eV and 4.85 eV for the C_{2v} and C_s pathways respectively [12]. Distortion along an out of plane b_1 coordinate retaining $\sigma(x, z)$ requires 6.7 eV, which is unfavourable in comparison with the b_2 pathway, in accord with the OCAMS result. The decomposition pathway on the ground state surface was recalculated using MCSCF [13], and SCF-CI with an extensive basis and large scale CI [14]. The latter study sets the activation energy at 3.76 eV. In both investigations, the transition state is found to be planar but highly assymmetric, and is characterized by one short and one long C-H bond [13, 14]. Such a distorted geometry can be achieved by superimposing upon the totally symmetric a_1 displacements a nuclear motion which is a linear combination of the two b_2 distortions depicted in Fig. 2. The normal coordinates of the transition state have also been calculated [13, 14]. Inspection of Fig. 4 of Ref. [14] indicates that the decomposition mode indeed retains planarity, but is unsymmetrical. The reaction coordinate thus only comprises symmetry coordinates which are totally symmetric (a') in C_s, the group characterizing the transition state, i.e. those which are of representations a_1 and b_2 in C_{2v}, the symmetry point group of the reactant. Accordingly, the qualitative aspects of the lowest energy pathway seem to be determined largely by the requirements of orbital symmetry.

2.2. The Excited State Reaction

Figure 1 can also be used to discuss the lowest energy path for process I on the first excited state potential energy surface. For this purpose we raise formaldehyde to its singlet or triplet n-π^* state, retaining C_{2v} symmetry, in which it is labelled $^1A_2$ or $^3A_2$ respectively. This lowest excited singlet (triplet) state of H_2CO is in fact pyramidal, with $C_s(xz)$ symmetry in its equlibrium geometry, [15], and is properly labelled $^1A''(^3A'')$. The formal retention of a group of higher symmetry in such cases has been justified theoretically [8b]. In the present instance $^1A_2(^3A_2)$ is the label in C_{2v} of the symmetric combination of the two pyramidal $^1A''(^3A'')$ states, or can be regarded as having been produced by Franck-Condon photoexcitation from the planar ground state, with enough vibrational energy to overcome the small inversion barrier of $\approx 2.(1.)$ kcal/mol [16].

Figure 1 indicates that the $^1A_2$ state correlates with a doubly excited state of the products; consequently, a path retaining C_{2v} geometry is symmetry forbidden. Following OCAMS, in an allowed photochemical process, the doubly and singly occupied orbitals have to correspond separately [8]. The doubly-occupied orbitals and the lower of the two singly-occupied orbitals correspond directly (see Fig. 1). The π^* $2b_1$ orbital of CH_2O, however, does not remain the highest singly occupied orbital along a C_{2v} path. The $6a_1$ σ orbital decreases significantly in energy and eventually becomes the $6a_1$ product orbital (see Fig. 1). If we require the system to remain on the first excited state surface all the way, we have to bring the $2b_1$ and $6a_1$ orbitals into induced correspondence. Thus, OCAMS proposes an out of plane b_1 distortion, towards a pyramidal geometry (see Fig. 2). As noted above, relaxation to the equilibrium geometry of the $^1A''(^3A'')$ state of formaldehyde is energetically negligible, so it is reasonable to conclude that the transition state is considerably more pyramidal [17].

The calculated $S_1(T_1)$ lowest energy path supports these qualitative conclusions. For a C_{2v} path on the $S_1(T_1)$ surface ~13 eV (14 eV) are required, whereas for a b_1 motion 9.0 eV (7.3 eV) are needed [12]. The potential energy barrier for process I along the excited state singlet pathway is, however, sufficiently high that internal conversion to S_0 and subsequent fragmentation along the ground state surface becomes competitive.

2.3. *Internal Conversion from S_1 to S_0 of Formaldehyde*

The internal conversion process, as can be deduced from the left side of Fig. 1, involves the transfer of an electron from a b_1 to a b_2 orbital. Therefore, a vibrational distortion of a_2 $(= b_1 \times b_2)$ symmetry is called for, but formaldehyde does not have any. However, such a distortion can be simulated by simultaneously exciting the b_1 and b_2 modes, thus providing a second order coupling term between the orbitals that transforms as a_2 $(= b_1 \times b_2)$ [8b]. This qualitative conclusion is fully supported by a theoretical analysis of the internal conversion from S_1 to S_0 of formaldehyde [18]: It is found that first order vibronic coupling matrix elements vanish due to symmetry. The only non-vanishing second order coupling matrix elements involve cross terms between the out of plane bending (b_1) mode and each of the non-totally symmetric in plane (b_2) vibrations, that between the two bending modes being the larger.

Reconsidering Fig. 1 as a correspondence diagram between reactant and product orbitals, we realize that the vibrations promoting the S_1 to S_0 conversion in formaldehyde are those which must be incorporated into the reaction coordinate, in order to allow a direct decomposition of S_1 formaldehyde to H_2 and CO in their ground states.

3. The Radical Decomposition Pathway

Another energetically feasible photochemical pathway is the rupture of one CH bond, designated as process II. Fig. 3 illustrates the effect on the energy of the molecular orbitals when this process is simulated, by elongating the C—H_2 bond (see Fig. 2) but preserving C_s symmetry. Fig. 3 indicates that the lowest energy path on the ground-state surface for process II can be expressed as an in plane motion, since all of the doubly occupied orbitals correspond directly. This process is, however, a homolytic bond rupture, which would be expected to be energetically more costly than the molecular fragmentation. Of more practical interest is the corresponding process on the excited state surface. Once more, excited formaldehyde is represented by the symmetric combination of the two non-planar excited states, but now classified in the reduced C_s symmetry as $^1A''(^3A'')$. The doubly-occupied orbitals and the singly occupied lone pair orbital $7a'$ correspond directly. However, remaining on the lowest excited state surface requires an induced correspondence between the $2a''$ π^* orbital of CH_2O and $8a'$ σ^* product orbital (see Fig. 3). This latter orbital is formed from the antibonding $8a'$ orbital of formaldehyde, which decreases significantly in energy [19]. Thus, OCAMS proposes an out-of-plane a'' distortion.

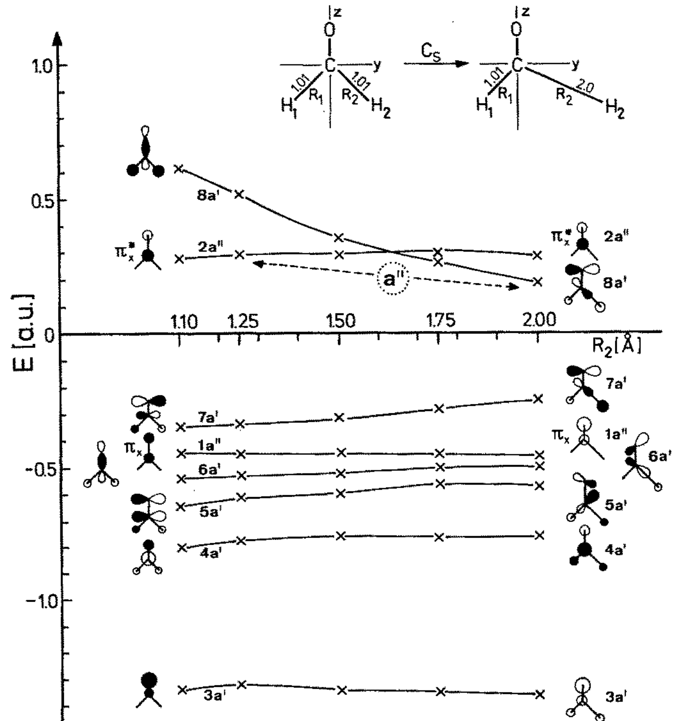

Fig. 3. Molecular orbital changes when the C—H_2 bond in formaldehyde is elongated, preserving the molecular plane. All other geometrical parameters remain at the experimental values [20]

These results are supported by *ab initio* calculations with limited CI and careful geometry optimization [19]. On the S_0 surface, atom H_2 (see Fig. 2) stays in the molecular $\sigma(y, z)$ plane when the C—H_2 distance is increased from 1.12 Å to 1.85 Å [19]. In the equilibrium geometry of $S_1(T_1)$, the C—H_2 bond with 1.10 Å (1.10 Å) length makes an angle of 60° (65°) with the x axis, in good agreement with the experimental values [19]. When the C—H_2 bond distance is increased to 1.85 Å, the angle with the x axis is only 20° (9°). Thus, the out of plane motion is an important component of the reaction coordinate of II along both the excited singlet and triplet surfaces.

4. Conclusion

The analysis of the various pathways for the decomposition of formaldehyde presented in this communication indicates that energetically favoured nuclear motions for the processes I and II can be deduced from considerations of orbital symmetry. This has been demonstrated for the ground- and excited state fragmentations and for internal conversion between the S_1 and S_0 surfaces as well. These results encourage the expectation that the nuclear motions preferentially involved in various photochemical and photophysical processes can be systematically singled out by symmetry considerations, applied at the molecular orbital level.

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