Theor Chim Acta (1987) 72: 35-46

Theoretica Chimica Acta

Self–consistent group calculations on a simple model for the photochemical α cleavage reaction of carbonyl compounds

Josef Schüle* and **Martin Klessinger**

Organisch-Chemisches Institut der Universitat, D-4400 Münster, Federal Republic of Germany

(Received July 12, 1986, revised April 7/Accepted April 30, 1987)

Potential energy surfaces were calculated for the ground and some excited states of formaldehyde as a model for the α cleavage reaction of carbonyl compounds. Computations were based on an STO-3G basis within the SCGF approach. Only planar geometries were considered. The VB-CI description of the group of electrons directly involved in the reaction allows for a general and illuminating discussion of the wave functions for this reaction and gives a theoretical justification of the configuration mixing model of Pross [8].

Key words: α Cleavage reaction of carbonyl compounds — Excited state potential energy surfaces — Photochemical reactions — VB-CI

1. Introduction

Although photochemical cleavage reactions are widely used, especially for the synthesis of strained molecules [1], many details of their mechanism are not yet completely understood. One of the most thoroughly studied photoreactions is the α cleavage of carbonyl compounds. As a first step towards a qualitative understanding of the structural requirements for this reaction, we present here the results of minimal basis set calculations of the ground and some excited state PES of formaldehyde as a simple model for more general α cleavage reactions.

Spectroscopy [2] and photochemistry [3] of formaldehyde have been extensively studied: It is now well established that the photofragmentation into molecular

---

* *Present address:* Institute of Theoretical Physics, University of Stockholm, S-11346 Stockholm, Sweden

products is a hot ground state reaction involving a barrier of nearly the same height as the total energy content of the photoexcited molecule. At wavelengths near 300 nm dissociation into radical products is observed. Numerous reports of theoretical studies on various states of formaldehyde occur in the literature. Model potential energy surfaces (PES) for the ground state have been derived [4], and features of ground and excited state wave functions such as dissociation energies and energy barriers for the dissociation to molecular or radical products and the rearrangement to hydroxycarbene have been the subject of very sophisticated calculations [5].

In the present paper we are aiming at a pictorial mapping of the ground and lowest singlet and triplet excited state PES of the radical dissociation reaction of formaldehyde which allows for a general discussion of α cleavage reactions of organic carbonyl compounds. As theoretically two kinds of products are to be discussed according to a ditopic and a tritopic reaction path [6] leading to bent and linear acyl radicals, respectively, we will give a representation of these surfaces as functions of the distance between the radical products and the valence angle of the acyl radical to be formed. Furthermore, we will give a detailed interpretation of the wave functions in order to establish a basis for a chemically illuminating discussion of the dependence of photochemical cleavage reactions on molecular and electronic structure. For that purpose, we choose the self-consistent group function (SCGF) approach [7]. This enables us to divide the total system up into different groups of electrons in such a way that one group comprises all electrons which are directly involved in the process of the reaction. The advantage of such a treatment is twofold:

(i) the six-electron problem is small enough to take into account full CI. This makes it possible to use the OAO-VB approach which lends itself much more naturally to chemical interpretation of the results than the usual MO approach.

(ii) the six-electron problem is the same for all α cleavage reactions, structural variations being taken into account through the effective Hamiltonian of this group.

Specifically, this approach will give a theoretical justification and form a basis for an extension of the configuration mixing model of Pross [8], which has proved rather successful in qualitative discussions of ground and excited state reactivities of organic molecules.

Based on the present results, a forthcoming paper [9] will further elaborate the relations between VB structures, spin eigenfunctions and barriers of potential energy hypersurfaces. By means of these concepts we will show that photochemical carbonyl reactions, such as α cleavage, H-abstraction and olefin addition, can be treated on a common footing.

2. Method of calculation

The SCGF method [7] is based on the generalized product approach [10], i.e.

the wave function

$$\Psi_{ab}(1,\ldots,N)=\mathscr{A}\Phi_{Aa}(1,\ldots,N_A)\Phi_{Bb}(N_A+1,\ldots,N_A+N_B)\ldots \tag{1}$$

is written as an antisymmetrized product of group functions, where Φ_{Rr} is a wave function for group R in state r. In this paper we use two types of group functions, closed shell one-determinant functions $\Phi_R(1,\ldots,N_R)$ built up from SCF-MOs

$$\varphi_i^R(1)=\sum_{\mu} c_{\mu i}^R \chi_{\mu}^R(1) \tag{2}$$

and VB-CI functions

$$\Phi_{Rr}(1,\ldots,N_R)=\sum_k C_k^{Rr}\phi_k^R(1,\ldots,N_R), \tag{3}$$

where the sum runs over all possible symmetry and spin-adapted VB structures $\phi_k^R(1,\ldots,N_R)$ which can be generated from a minimal basis. The physical significance of the separability of the electrons into different groups of electrons rests on the strong orthogonality relation [11]

$$\int \Phi_{Rr}^*(1,i,j,\ldots)\Phi_{Ss}(1,k,l,\ldots)\,d\tau_1=0 \text{ for } R\neq S \text{ and } r\neq s, \tag{4}$$

which is satisfied by constructing the Φ_{Rr} from different sets of orthogonal hybrid AOs χ_{μ}^R. The latter are obtained from Gaussian AOs by a symmetric Löwdin orthogonalization after Schmidt orthogonalizing the symmetrically orthogonalized inner shell orbitals and by a transformation to hybrid AOs [12]. As a consequence, the results are dependent on the partitioning of the AO basis into different sets $\chi_{\mu}^R,\ldots,\chi_{\nu}^S,\ldots,$ for groups $R, S, \ldots$. Hybridisation, which generates these different sets, has therefore to be optimized for each geometry to be calculated. This was done with an accuracy of $1\cdot 10^{-5}$ a.u. by minimizing the total energy with respect to hybridization. The general form of the hybrid AOs and the type of the group functions, used to treat the α cleavage reaction of formaldehyde, are indicated in Table 1.

The SCGF approach is exactly analogous to the usual MO procedure, except that each electron in its MO is now replaced by a group of electrons described by a many-electron function; the best approximation is that which minimizes the energy for each group in an effective field provided by the other groups. This

Table 1. Groups of electrons and group functions used for calculated on the α cleavage of formaldehyde

R	No of electrons	$\chi_{\mu}^R(i)$[a]	$\Phi_{Rr}(1,\ldots,N_R)$
1	6	x_O, y_O, y_C, b_1, h_a	VB-CI (Eq. (3))
2	4	o, c	One-determinant
3	6	s_O, z_O, b_2, b_3, h_b	One-determinant

[a] s_A, x_A, y_A and z_A denote $2s$, $2p_x$, $2p_y$ and $2p_z$ AOs centered at A; o, c, h_a and h_b denote the $1s$ AOs of O, C, H_a and H_b respectively and b_i are bond hybrids at C defined by $b_i=1/\sqrt{\kappa_i^2+\lambda_i^2+\mu_i^2}\,(\kappa_i s_C+\lambda_i x_C+\mu_i z_C)$; for the orientation of the axes see Scheme 1

leads to an eigenvalue problem

$$H_{\mathrm{eff}}^{R} C^{Rr} = E_R C^{Rr} \tag{5}$$

for each group [7]. The effective Coulomb exchange field operating on any group R, is determined by knowing the charge density matrices

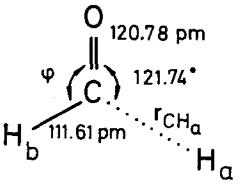
$$P_1^S(ss) = \sum_{k,l} C_k^{Ss} C_l^{Ss} p_1^S(kl) \tag{6}$$

for the other groups S in their state s. In the actual calculation it is these matrices which are revised iteratively until self-consistency is achieved, while the transition densities $p_1^S(kl)$ had to be evaluated only once for the VB structures of the six-electron problem (cf. [7]). Locally excited states of the six-electron group R corresponding to n, π^* and π, π^* excitations, are obtained from higher eigenvalues of Eq. (5), which again has to be solved iteratively for all groups in a self-consistent way. The SCGF formalism has been incorporated [13, 14] into a version of the GAUSSIAN 76 program [15].

3. Results

3.1. *Potential energy surfaces*

Using a minimal STO-3G basis, the PES of the ground state (S_0), the (n, π^*)-excited singlet and triplet states (S_a and T_a) and the (π, π^*)-excited triplet state (T_s) were calculated for $H_aH_bC{=}O$ as a function of the C-H_a distance $r_{CH_a} =$ 111.61–411.61 pm ($\Delta r = 0$–300 pm) and the OCH_b angle $\varphi = 90$–180° with all other distances and angles taken from the experimental r_e-structure [16] shown in Scheme 1. Thus, no geometry optimization was performed, and C_s symmetry is retained throughout. This reduces considerably the number of symmetry adapted VB structures which have to be taken into account for each state. With respect to the molecular plane the wave functions are therefore symmetric (s) as S_0 ($^1A'$) and $T_s(^3A')$ or antisymmetric (a) as $S_a(^1A'')$ and $T_a(^3A'')$. Figure 1 gives a three-dimensional plot of these four PES, obtained from a net of 11 · 17 points, and in Fig. 2 contour plots are shown for each of these states. Two cross-sections, through the PES of Fig. 1, are important for the discussion of the α cleavage reaction: On the antisymmetric PES S_a and T_a the reaction path corresponds to a change of the OCH_b angle from $\varphi = 120°$ to $\varphi = 180°$ as indicated in Fig. 2b, c by a broken line; the corresponding cross-section is given in Fig. 3. For a reaction on S_0 and T_s, φ remains nearly constant, so that an appropriate cross-section is given by the side-view of Fig. 1. In Fig. 4 finally the two triplet PES are plotted in such a way as to show clearly their intersection which occurs due to the C_s



Scheme 1

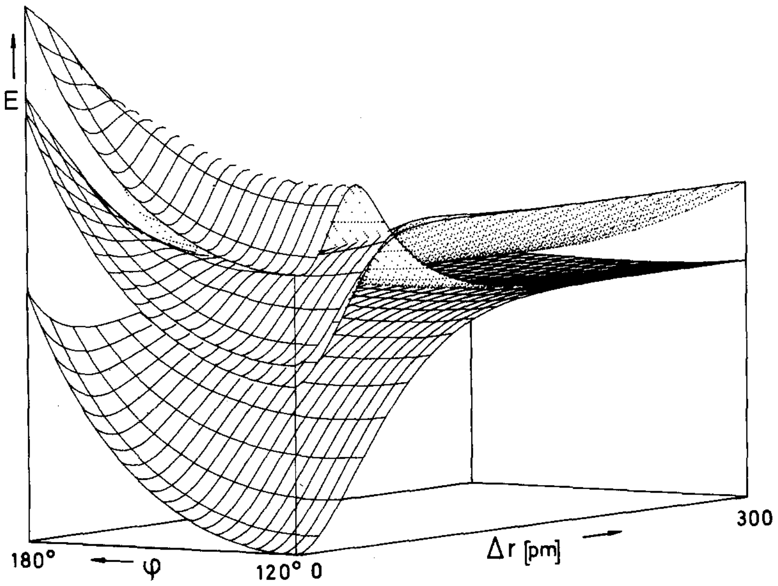


Fig. 1. Potential energy hypersurfaces for planar formaldehyde plotted as a function of the distance r_{CH_a} and the OCH$_b$ angle φ. At short distances the ordering of states is S_0, T_a, S_a, T_s

symmetry of the problem. In Table 2 some of the calculated data are compared to results from the literature.

The energy of the ground state S_0 increases from the minimum near the experimental equilibrium geometry both with increasing distance r_{CH_a} as well as with increasing OCH$_b$ angle φ; at large distances ($\Delta r \geq 300$ pm) a shallow minimum occurs at $\varphi = 145°$. From Table 2 it is seen that the calculated dissociation energy $E_D(S_0) = 453.9$ kJ/mol is much higher than the experimental value $E_D^{\mathrm{exp}}(S_0) = 366.1$ kJ/mol [17] and other theoretical values. At large distances the symmetric states S_0 and T_s are degenerate as is to be expected from correlation diagrams [6a].

The S_a and T_a surfaces lie very close to each other and are degenerate at larger distances, where they decrease in energy with increasing φ, so that for $\varphi = 180°$ all four surfaces are degenerate. Both S_a and T_a show a barrier, which for increasing φ, is shifted to smaller r_{CH_a} distances and which has a saddlepoint at $\Delta r_{\mathrm{CH}_a} = 170$ pm and $\varphi = 150°$. At the equilibrium geometry T_a lies below S_a, but along the reaction coordinate, these two states cross before reaching the top of the barrier (Fig. 3). Therefore, the barrier height in the triplet state $\Delta E(T_a) = 217.7$ kJ/mol is larger than $\Delta E(S_a) = 171.4$ kJ/mol for the singlet state, which in turn is larger than the value calculated by Hayes and Morokuma [18] as a result of the rigid geometry and the basis set used in our calculations (cf. Table 2). The calculated barrier height for the recombination reaction of the linear acyl radical and the H atom is $\Delta E_R(S_a) = 86.0$ kJ/mol and $\Delta E_R(T_a) = 90.0$ kJ/mol, respectively.

The T_s state shows a steep and narrow barrier, for which the minimum height

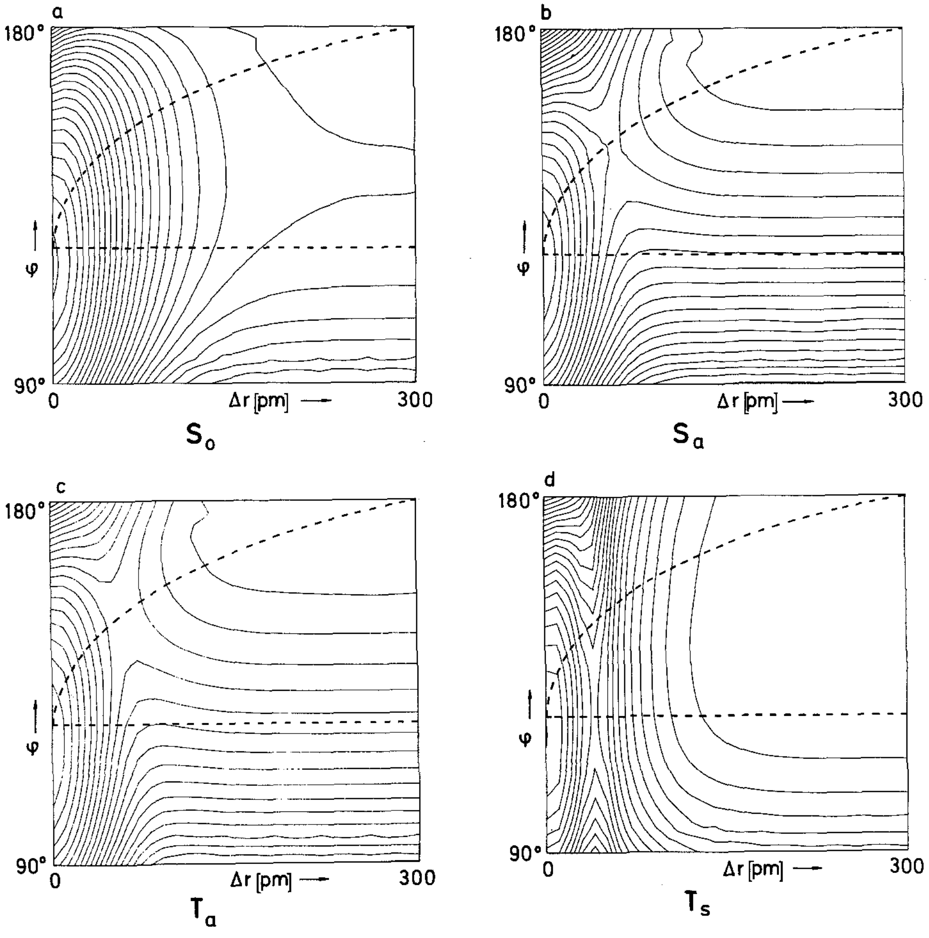


Fig. 2a–d. Contour diagrams of the formaldehyde potential energy surfaces. **a** Ground state S_0; **b–d** excited states S_a, T_a and T_s, respectively

is $\Delta E(T_s) = 160.5$ kJ/mol and thus appreciably lower than $\Delta E(S_a)$ and $\Delta E(T_a)$. For long distances there is again a shallow minimum at an OCH_b angle $\varphi = 145°$. Due to the assumed C_s symmetry the crossing of the two triplet states T_s and T_a is not avoided. From Fig. 4 it is seen for $\varphi = 120°$ that the crossing occurs before the top of the barrier in T_a is reached, so that for such a geometry internal conversion from T_a to T_s could reduce the barrier of the reaction starting on the T_a surface. With increasing OCH_b angle φ, however, the crossing of the T_a and T_s states is shifted in such a way that it occurs at longer distances r_{CH_a} than the barrier in T_a; at large values of r_{CH_a} and φ the two states are degenerate.

3.2. Wave functions

In Fig. 5 the coefficients of the various VB structures are plotted as a function of the reaction coordinate for all four states considered. Only the results for

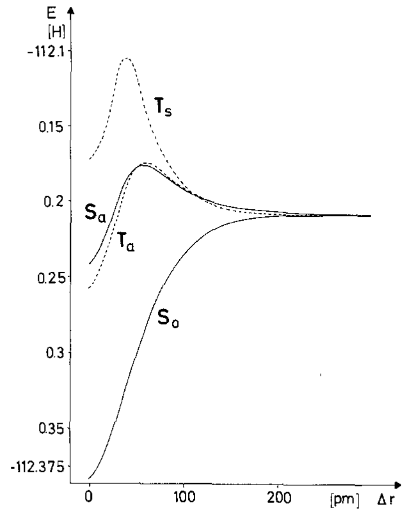


Fig. 3. Cross section through the formaldehyde potential energy surfaces corresponding to the reaction leading to a linear formyl radical

constant OCH_b angle $\varphi = 120°$ are shown, as those for the reaction path leading to a linear acyl radical differ only slightly. Before we discuss these results in details, two remarks may be useful. First, it has been known since the early work of Slater [20] that the use of OAOs requires Heitler-London as well as ionic VB structures in order to describe covalent bonding, so that in OAO calculations the contribution of ionic structures is overemphasized at the expense of covalent structures [21]. Secondly, in order to relate the VB results to more common MO pictures, MO configurations based on localized MOs can be expanded in terms of VB structures according to $|\phi\bar{\phi}| = |(a+b)(\bar{a}+\bar{b})| = |a\bar{a}| + |b\bar{b}| + (|a\bar{b}| + |b\bar{a}|)$. In what follows the VB structures a^2, b^2 and (ab) are said to belong to the *MO* configuration ϕ^2.

From Fig. 5a it is seen that the structure 1 is predominant in the groundstate wave function $\Psi(S_0)$ for all values r_{CH_a}. Small contributions come from structures

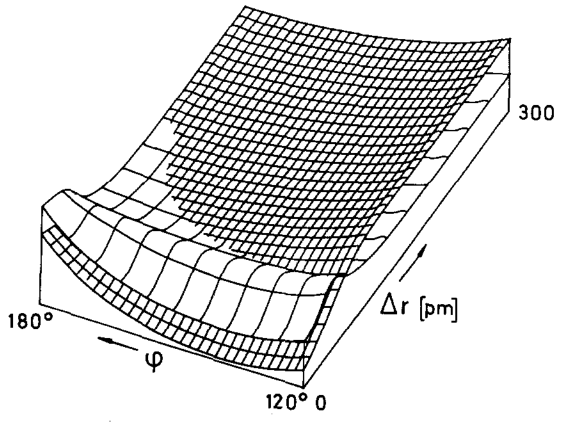


Fig. 4. The two lowest triplet excited potential energy surfaces T_a and T_s of formaldehyde

Table 2. Dissociation and excitation energies of formaldehyde as well as minimum barriers for α cleavage reaction (in kJ/mol)

			Calculated			
State	This work	Exp.[a]	STO[b]	STO-3G[c]	DZ[d]	MBPT[e]
Dissociation energy						
S_0	453.9	366.1	424.5	—	391	361.7
Excitation energies						
$S_a(n, \pi^*)$	373.7	337.2	281.7	—	—	373.9
$T_a(n, \pi^*)$	331.5	301.2	247.0	368.6	—	352.9
$T_s(\pi, \pi^*)$	554.3	—	—	572.1	—	—
Minimum barrier for reaction						
S_a	171.4	—	—	—	—	—
T_a	217.7	—	140.9	—	—	—
T_s	160.5	—	—	120.5	—	—

[a] [17]
[b] [18]
[c] [19]
[d] [5a]
[e] [5d]

2, 3, 4 and 5 which all belong to the MO configuration $n^2\pi^2\sigma^2$. It is quite easy to understand that the extent to which 2 and 3 with charge separation in the CH_a bond contribute to $\Psi(S_0)$ decrease with increasing r_{CH_a}, whereas the contributions of 4 and 5 with charge separation in the CO π bond remain approximately constant. Structures 6 and 7, which contribute significantly only at larger r_{CH_a}, belong to an excited MO configuration $n\pi^2\sigma^2\sigma^*$.

Figures 5b and c are very similar to each other, and are described by the same VB structures, except that the two unpaired electrons have antiparallel spins in Fig. 5b, which describes the singlet wave function $\Psi(S_a)$, but they have parallel spins in Fig. 5c, which describes the triplet wave function $\Psi(T_a)$. In contrast to Fig. 5a, the main contributions to the wave functions $\Psi(S_a)$ and $\Psi(T_a)$ come from two VB structures 8 and 9, with 8 dominating at small r_{CH_a} values and the other (9) at large r_{CH_a} values. The broken lines in Fig. 5b, c give the weighted sum of the coefficients of 8 and 9, which takes into account the metric, as these two structures are not orthogonal (for details see [9]). The r_{CH_a} dependence of the minor contributions from 10, 11 and 12 is again as expected; the structures 13, 14 and 15 which come in at larger r_{CH_a} values belong to higher excited MO configurations.

At a first sight Fig. 5d with two main structures 16 and 17 for the T_s state, one dominating at short distances and the other one at larger distances, and with minor contributions which show the expected r_{CH_a} dependence looks very similar to Fig. 5b, c. But there is a very important difference: in contrast to the two dominating structures 8 and 9 of T_a and S_a, the main structurs 16 and 17 of T_s

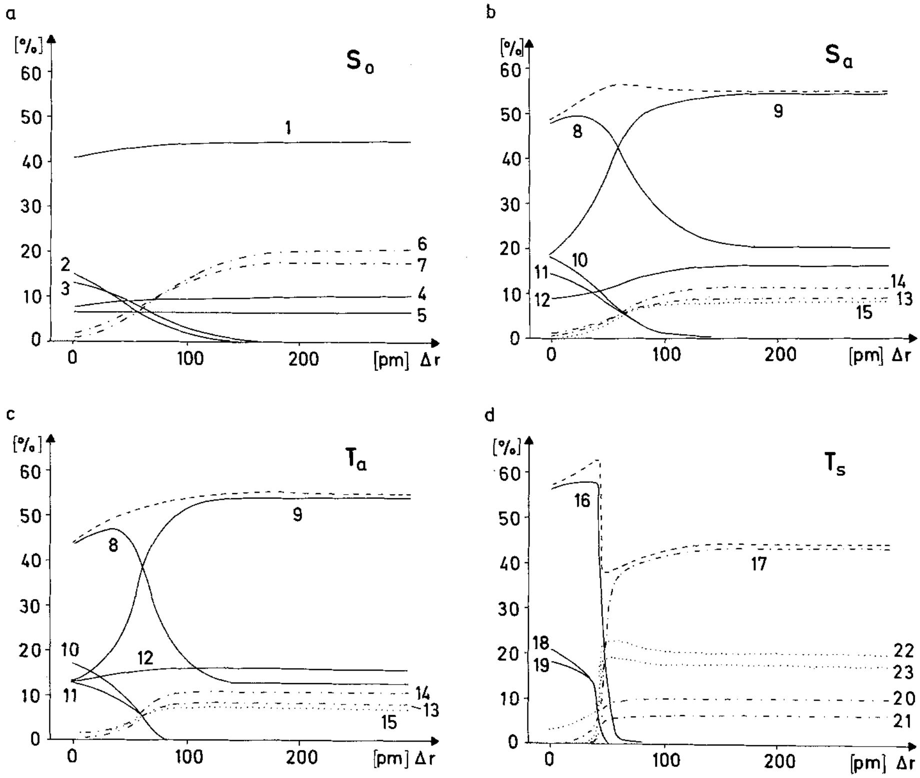
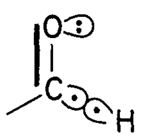


Fig. 5a–d. Contributions of the various VB structures to the formaldehyde wave functions. **a** The ground state S_0; **b–d** the excited states S_a, T_a and T_s, respectively (different line types are used for VB structures corresponding to the different MO configurations)

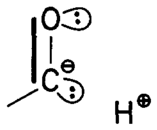
are mutually exclusive, i.e. at small and large distances, respectively, the contribution of one or the other structure is practically zero, and the crossing region is very narrow. This is closely connected with the fact that 16 and 17 are orthogonal and belong to different MO configurations $n^2\pi\pi^*\sigma^2$ and $n^2\pi^2\sigma\sigma^*$, respectively. This point will be considered in more detail in a forthcoming paper [9].

4. Discussion

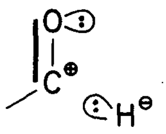
From the comparison with earlier results of theoretical calculations for the α cleavage given in Table 2, we may conclude that the PES, depicted in Figs. 1 and 2, provide a qualitatively correct description of this reaction in spite of the approximations implicit in our treatment, i.e. rigid geometry, minimal basis, and the SCGF formalism. This is confirmed also by a comparison with the PES obtained for the same system by semiempirical MNDOC-CI calculations [22]. It is known experimentally that formaldehyde undergoes a photochemical α cleavage reaction only at higher excitation energies [23]. This is in agreement with the high barriers obtained from the present calculations. As could be confirmed by MNDOC calculations [22], it is a fair assumption that the heights



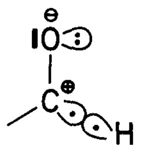
1



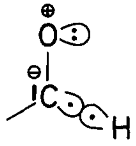
2



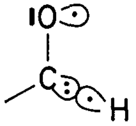
3



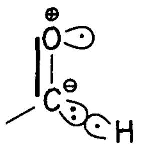
4



5

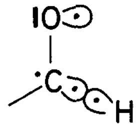


6

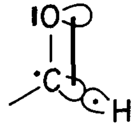


7

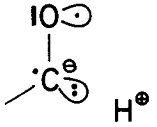
of the barriers are very much dependent on the nature of the substituents R_a and R_b at the carbonly group, but the general shape of the PES is largely independent of the actual molecule under consideration. Thus, we may conclude that reaction products are linear if they develop in the T_a or S_a state, and bent in the S_0 and T_s state. Furthermore, the T_a and S_a PES are very close to each other and show a barrier with a saddle point at $r_{\mathrm{CH}_a} = 170$ pm and $\varphi = 150°$. Finally, the crossing between the two triplet states, which is avoided in the nonplanar case, is of



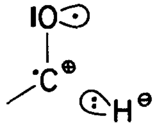
8



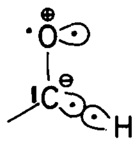
9



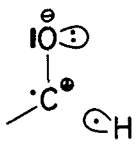
10



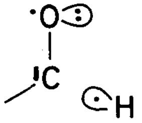
11



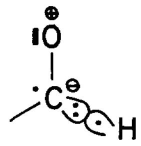
12



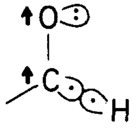
13



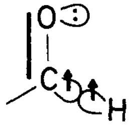
14



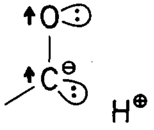
15



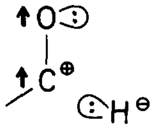
16



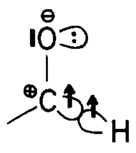
17



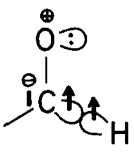
18



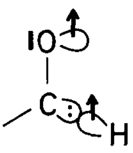
19



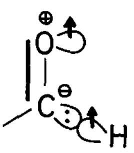
20



21



22



23

particular importance. The outcome of a reaction, starting on the $^3(n, \pi^*)$ excited state T_a, will very much depend on whether or not the barrier is reduced by the (avoided) crossing between T_a and T_s, i.e. whether the crossing occurs at larger or at smaller distances than the barrier in T_a. From the present result, no such reduction of the barrier is to be expected in the case of formaldehyde (cf. Fig. 3, 4).

The analysis of the wave function in terms of VB structures shows that there is just one structure dominating the wave function $\Psi(S_0)$ of the ground state S_0, which has no barrier, whereas there are two structures dominating the wavefunctions $\Psi(T_a)$, $\Psi(S_a)$ and $\Psi(T_s)$ of the excited states. As the energy of one of these structures increases along the reaction coordinate, the energy of the other one decreases; this illustrates in a rather illuminating way the origin of the barrier. In fact, the position of the barriers in Fig. 2b–d agrees very well with the geometry at which the contributions of the two structures to the excited state wave function are equal and at which the corresponding curves in Fig. 3b–d cross. These results are very much in line with the configurational mixing model of Pross [8] and can be taken as a confirmation of the validity of that model. It may also be noted, that the shape of the barrier, i.e. whether it is wide and low or narrow and high, is closely connected with the question of whether the two dominating structures are orthogonal or not. A detailed treatment of this aspect in terms of spin eigenfunctions will be given in a forthcoming paper [9].

Acknowledgment. Financial support by the "Verband der Chemischen Industrie" through a doctoral scholarship to one of us (J.S.) is gratefully acknowledged.

References and notes

1. (a) Turro NJ (1978) Modern molecular photochemistry. Benjamin/Cummings, Menlo Park; (b) for special examples cf. Katz TJ, Acton NJ (1973) J Am Chem Soc 95:2738; Maier G, Pfriem S, Schäfer U, Matusch R (1978) Angew Chem 90:552
3. Cloutier DJ, Ramsay DA (1983) Ann Rev Phys Chem 34:31; cf. also Suto M, Lee LC (1986) J Chem Phys 85:4228
3. Moore CB, Weisshaar JC (1983) Ann Rev Phys Chem 34:525; Debarre D, Lefebvre M, Pialat M, Taran JPE, Bamford DJ, Moore CB (1985) J Chem Phys 83:4476
4. Carter S, Mills IM, Murrell JN (1980) Mol Phys 39:455; cf. also Murrell JN, Carter S, Farantos SC, Huxley P, Varandas AJC (1984) Molecular potential energy functions. Wiley, Chichester
5. (a) Goddard JD, Schaefer HF (1979) J Chem Phys 70:5117; (b) Goddard JD, Yamaguchi Y, Schaefer, HF (1981) J Chem Phys 75:3459; (c) Frisch MJ, Krishnan R, Pople JA (1981) J Phys Chem 85:1467; (d) Adams GF, Bent GD, Bartlett RJ, Purvis GD (1981) J Chem Phys 75:834; (e) Dupuis M, Lester WA, Lengsfield BH, Liu B (1983) J Chem Phys 79:6167, and earlier references quoted in these papers
6. (a) Salem L (1974) J Am Chem Soc 96:3486; (b) Dauben WG, Salem L, Turro NJ (1975) Acc Chem Res 2:41
7. Klessinger M, McWeeny R (1965) J Chem Phys 42:3343
8. Pross A (1985) Adv Phys Prg Chem 21:99; (1985) Acc Chem Res 18:212
9. Schüle J, Klessinger, M: To be published
10. McWeeny R (1960) Rev Mod Phys 32:335
11. Löwdin PO (1961) J Chem Phys 35:78
12. Klessinger M (1975) J Chem Phys 43:117
13. Schüle J (1986) Dissertation, Münster
14. Zywietz A (1984) Dissertation, Münster
15. Binkley JS, Whiteside RA, Hariharan PC, Seeger R, Pople JA, Hehre WJ, Newton MD (1976) Gaussian 76 QCPE 368
16. Takagi K, Oka T (1963) J Phys Soc Jpn 18:1174
17. Houston PL, Moore CB (1976) J Chem Phys 65:757
18. Hayes DM, Morokuma K (1972) Chem Phys Lett 12:539
19. Grimbert D, Salem L (1976) Chem Phys Lett 43:435
20. Slater JC (1951) J Chem Phys 19:220
21. Cook DB (1978) Struct Bonding Berlin 35:37
22. Reinsch M, Höweler U, Klessinger M (1987) Angew Chem 99:250
23. Moortgat GK, Seiler W, Warneck P (1983) J Chem Phys 78:1185