

MNDOC-CI CALCULATIONS FOR ORGANIC PHOTOREACTIONS. I. THE α -CLEAVAGE REACTION OF CARBONYL COMPOUNDS

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MNDOC-CI results are reported for the photochemical α -cleavage reaction of carbonyl compounds. Potential energy surfaces for some excited singlet and triplet states and cross-sections along the bitopic reaction path show that the activation energy of the α -cleavage reaction is determined by the relative energetic position of the lowest two triplet states. The reactivity of aliphatic ketones depends only on the degree of branching at the α -carbon, because the triplet barrier is due to an (avoided) crossing of two surfaces corresponding to an $n\pi^*$ and $\pi\pi^*$ excitation respectively, which correlates with the stability of the leaving alkyl radical. For conjugated carbonyl compounds, on the other hand, the position of the crossing point is independent of the ${}^3n\pi^*$ excitation energy, but if the ${}^3\pi\pi^*$ surface is below the ${}^3n\pi^*$ surface all the way along the reaction coordinate, the reaction is determined by the barrier on the ${}^3\pi\pi^*$ surface and any additional stabilization of the ${}^3\pi\pi^*$ state increases the barrier.

INTRODUCTION

Semi-empirical methods have been very successful in calculating ground-state properties and reactivities of organic molecules.¹ Even *ab initio* results for transition-state geometries and energies could be reproduced very well by using suitably adapted semi-empirical methods.² On the other hand, applications to excited-state properties and photoreactions have been scarce up to now,³⁻⁶ the reasons being fairly obvious: the discussion of photoreactions requires a knowledge of more than one potential energy surface, each of which has to be calculated over large regions, as the spectroscopic and reactive minima may be located in different parts of these surfaces. Most important, even the spectroscopic minima close to the ground-state equilibrium geometry cannot be described properly without taking into account the configuration interaction, which may be even more important for the barriers and the reactive minima further away from these geometries. However, as the parametrization of semi-empirical methods refers to the SCF level and takes into account correlation effects, CI would result in taking into account some of the correlation effects twice.

Some years ago, Thiel⁷ gave a parametrization of the MNDO method designed to take into account correlation effects explicitly. Based on this MNDOC method of Thiel⁷ and the DZDO program of Downing *et al.*,⁸ we developed the MNDOC-CI program system^{3,9} for

semi-empirical calculations of excited-state properties. One of the main features of this program is the flexibility in selecting configurations in order to limit the CI problem to dimensions which are reasonable in connection with a semi-empirical method of calculation.^{3,9} After having shown that it is possible to select the configurations in such a way that all states of interest are being described with sufficient and equal accuracy without undue computational efforts,⁹ we now present a first application of the method to photoreactions in order to discuss the structural dependence of mechanism and reactivity. For this first application we choose the photochemical α -cleavage reaction of carbonyl compounds, which has been studied experimentally very thoroughly¹⁰⁻²² and for which several *ab initio* calculations²³⁻²⁹ and some semi-empirical calculations^{6a-c} have been published. Thus detailed comparisons make it possible to assess the quality of our results.

METHOD OF COMPUTATION

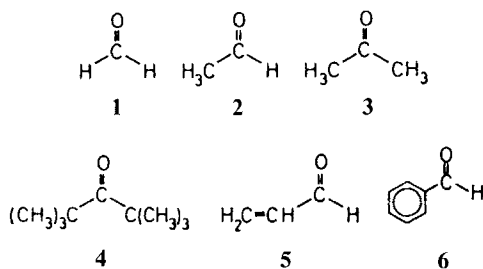
The SCF part of the MNDOC-CI program is identical with the MNDOC program of Thiel⁷ (cf. QCPE 438), whereas for the CI calculations the DZDO program,⁸ which is based on the formalism of Harris³⁰ for evaluating the matrix elements, was extended to include various criteria for selecting configurations, of which the excitation indices³¹ and the active space are of particular importance. The PC version of the program can handle up to 90 configurations, whereas an extended

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version is designed for up to 500 configurations, which can be selected from all configurations singly and doubly excited with respect to one or more (up to six) reference configurations. Most results described in this paper were obtained from 200 configurations with different reference configurations for each state built up from the closed-shell ground-state MOs and from half-electron triplet MOs,³² respectively. The CI space is truncated by means of the excitation indices for which a value of 4/8, referring to the maximal differences of orbital indices for single and double excitations, respectively,⁹ was chosen for most of the molecules considered.

RESULTS

Some representative results for the ground-state (S_0) energy at the standard geometry and the vertical excitation energies (ΔE) to the lowest singlet state, S_a , and the lowest two triplet states, T_a and T_s , of formaldehyde (1), acetaldehyde (2), acetone (3), di-*tert*-butyl ketone (4), acrolein (5) and benzaldehyde (6) are collected in Table 1 together with some experimental data and *ab initio* results. The MNDOC results in Table 1 were obtained for planar systems and the subscripts indicate the symmetry behaviour with respect to reflection on this plane. In the ground-state equilibrium geometry the T_s state corresponds to $\pi\pi^*$ and the T_a and S_a states to $n\pi^*$ excitation.



In Figure 2 the energies of the ground state S_0 and of the excited states T_a , T_s and S_a of planar acetaldehyde (2) and benzaldehyde (6) are plotted against the distance R_{CH} between the leaving H atom and the carbonyl carbon and the angle $\angle OCC$ (cf. Figure 1 for the definition of the geometry variables). From this diagram it is seen that for the symmetric states S_0 and T_s the bent geometry of the acyl radical is more stable, so that the reaction on these surfaces follows a ditopic reaction path.³⁵ For the antisymmetric states T_a and S_a the preferred acyl radical geometry is linear for sufficiently large R_{CH} , and all four states (S_0 , S_a , T_a and T_s) are degenerate, as is to be expected for a tritopic reaction.³⁵

A cross-section through the potential energy surfaces along the ditopic reaction path is shown for acetaldehyde (2), acrolein (5) and benzaldehyde (6) in

Figure 3. In the case of acetaldehyde (2), the α -cleavage reaction will start from an $n\pi^*$ excited species on the T_a surface and will end up at the geometry of the bent acyl radical on the T_s surface (cf. Figure 2a), which at large distances is dominated by an $n\sigma^*$ configuration. Owing to the early crossing of the two triplet states at $R_{CH} \approx 160$ pm and $\angle RCO \approx 135^\circ$, the α -cleavage reaction can be well described as proceeding along the bitopic path. In the singlet state, on the other hand, the $n\pi^*$ excited species will stay on the S_a surface and the reaction will follow the tritopic path. This reaction is expected to be much less efficient than the triplet reaction, because there is no (avoided) crossing which could reduce the barrier on the S_a surface and because there is no barrier for the back-reaction between the singlet biradical and the educt ground state.

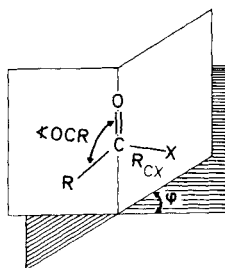
The cross-sections for the α -cleavage reaction of acrolein and benzaldehyde (Figures 3b and c) show the influence of conjugation on the barrier height of the α -cleavage reaction. Whereas at the equilibrium geometry the T_s state is considerably stabilized by conjugation for both compounds, the energetic position of the T_s barrier is not affected, as is to be expected from the fact that this barrier is due to an avoided crossing of the $\pi\pi^*$ and the $n\sigma^*$ states.^{36,37}

Consequently, the crossing between the T_a and T_s surfaces occurs for acetaldehyde and acrolein at similar distances and energies, because the energy of the T_s state at the crossing point is determined primarily by the top of the barrier and not by the energy at equilibrium geometry. For benzaldehyde the calculated T_s surface remains below the T_a surface all the way along the cross-section and the triplet barrier height is given by the corresponding T_s barrier. The fact that there is no avoided crossing of the T_a and T_s surfaces which could reduce the barrier in the lowest triplet state gives an explanation for the lower reactivity of conjugated compounds which has been observed experimentally.^{21,22} The MNDOC-CI results for *p*-methoxy- and *p*-phenylbenzaldehyde show that further stabilization of the T_s state even increases the T_s barrier by 27 and 40 kJ mol⁻¹, respectively.

Table 2 shows the dissociation energies (E_D) for the ground state and the energy barriers (E_B) for the α -cleavage reaction in the excited states S_a , T_a and T_s , which are determined by the difference of the maximum energy value along the reaction coordinate and the energy at the educt equilibrium geometry for each state, respectively (cf. Figure 3a). The barrier heights for the T_a and S_a states are very similar for all molecules, whereas the barrier in the T_s state is small except for acrolein and benzaldehyde. The energy E_{CP} at the crossing point (CP) of the T_a and T_s surfaces gives an upper limit for the activation energy E_a in the lowest triplet state, whereas for benzaldehyde there is no crossing point and the triplet activation energy can be estimated by the corresponding $E_B(T_s)$ value (cf. Figures 2b and 3c).

Table 1. Ground-state CI energies, E_0 , and vertical excitation energies, ΔE , for S_a , T_a and T_s of carbonyl compounds with planar geometries

Compound	Ground-state energy, E_0 (a.u.)	Excitation energy (kJ mol^{-1})		
		ΔE (S_a)	ΔE (T_a)	ΔE (T_s)
Formaldehyde (1)	-17.4707	275	241	425
		282 ^a	247 ^a	
		374 ^b	332 ^b	554 ^b
Exp.		337 ^c	301 ^c	560-600 ^c
Acetaldehyde (2)	-23.2025	305	277	485
			166-322 ^d	
Exp.			367 ^e	613 ^e
Acetone (3)	-28.9410	215	191	390
Di- <i>tert</i> -butyl ketone (4)	-63.3185	192	165	350
Acrolein (5)	-27.8247	256	253	306
Benzaldehyde (6)	-47.5870	270	261	235

^a Ref. 23.^b Ref. 24.^c Ref. 33.^d Ref. 26a.^e Ref. 34.Figure 1. Definition of geometry parameters for the description of the α -cleavage reaction

From an analysis of the wavefunction of formaldehyde for various points along the reaction path shown in Table 3, it is seen that the antisymmetric states are described reasonably well by a single configuration ($n\pi^*$) up to $R_{CH} = 150$ pm. One σ MO rises with increasing R_{CH} until it is degenerate with the π orbital, whereas the corresponding σ^* orbital is stabilized such that for distances greater than 150 pm it is below the π^* MO. This MO interchange leads to an increased importance of those two singly excited configurations which have a singly occupied σ^* or σ MO, respectively. For the symmetric triplet state T_s the $\pi\pi^*$ reference configuration is replaced by an $n\sigma^*$ configuration at this distance. With increasing distance the energy of the closed shell reference configuration for the S_0 state increases in energy corresponding to an ionic structure $H^- + HCO^+$ and at biradicaloid geometries ($R_{CH} = 300$ pm) S_0 is predominantly described by an open-shell configuration, which therefore has been chosen as reference at these geometries. For all states, configurations which are doubly excited with respect to

the reference configuration are of negligible importance except for the S_0 closed-shell reference at great distances, i.e. 160–250 pm.

If the non-planarity of the reaction system is taken into account, the symmetry labelling of states is no longer possible. The lowest triplet state, which is of particular interest for the reaction, is now called T_1 . In order to obtain some idea of the geometry changes during the reaction, the geometry of this T_1 state was optimized at the SCF level using half-electron orbitals. Some of the results for formaldehyde are shown in Fig. 4. It is seen that the T_1 state is pyramidal at the equilibrium geometry ($\varphi = \angle H_aCOH_b - 180^\circ = 40^\circ$). With increasing distance, this effect is even more pronounced and in the transition-state geometry the leaving H_a is in a position almost perpendicular to the COH_b plane. Along the reaction coordinate $\angle COH_b$ changes from 118° to 135° , while the CO bond length is reduced from 127.9 to 116.9 pm owing to its triple bond character in the acyl radical. As is to be expected, the value of 129 kJ mol^{-1} for E_a is smaller than the energy of the T_a and T_s crossing point ($E_{CP} = 145 \text{ kJ mol}^{-1}$, cf. Table 2). The vertical and adiabatic excitation energies for the S_1 and T_1 states and the S_0 and S_1 equilibrium geometries are also shown in Figure 4.

Similar data for acetaldehyde are collected in Table 4. The optimized MNDOC geometries are in good agreement with *ab initio* results.²⁶ At its equilibrium geometry the T_1 state is calculated to be non-planar and the leaving group is almost perpendicular to the plane of the acyl fragment in the transition-state geometry. The changes in the CO bond length and the bond angle in the acyl fragment are similar to those of formaldehyde (cf. Tables 4 and 5). If the methyl group is the leaving group, it is almost planar in the transition-state

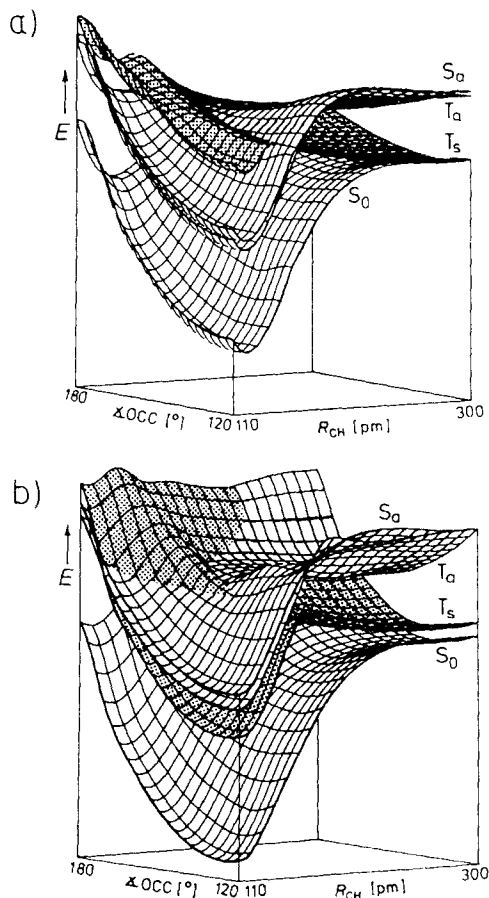


Figure 2. Potential energy surfaces of the ground state S_0 and of the excited states T_s , T_a and S_a of (a) planar acetaldehyde and (b) benzaldehyde plotted against the distance R_{CH} and the angle $\angle OCC$. (For steric reasons the acyl radical can be linear only at distances R_{CH} larger than those shown)

geometry, and in contrast to the S_0 state it prefers a staggered conformation ($\tau = \angle H_m CCO \approx 60^\circ$). The activation energies calculated for the optimized triplet geometries (Table 5) for the cleavage of the methyl group (153 kJ mol^{-1}) and the hydrogen atom (138 kJ mol^{-1}) show a greater deviation from the energy E_{CP} of the crossing point of the T_a and T_s surfaces (Table 2) than in the case of formaldehyde; this is due to the greater importance of relaxation effects for the methyl group in the transition state geometry (cf. ΔE_{opt} in Table 5). The energy of the SCF configuration is lowered by 5 kJ mol^{-1} by CI at the equilibrium geometry and changes considerably along the optimized T_1 reaction path (Table 5). However, CI leads to a negligible decrease in the activation energy (ca 7 kJ mol^{-1}), because the lowering of energy is comparable in the equilibrium and the transition-state

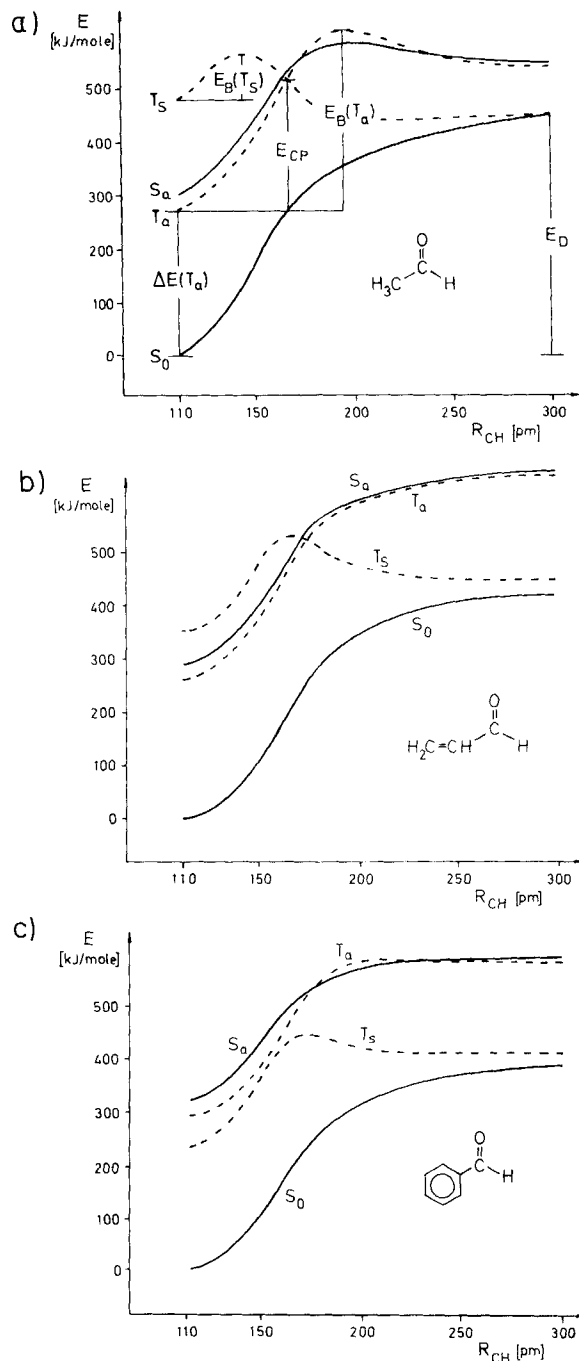


Figure 3. Cross-section through the potential energy surfaces of (a) acetaldehyde, (b) acrolein and (c) benzaldehyde along the ditopic reaction path for the planar α -cleavage reaction of the H atom. The definition of dissociation energy E_D , excitation energies ΔE , excited state barriers E_B and the energy E_{CP} of the T_s - T_a crossing point is indicated in (a)

Table 2. Dissociation energy, E_D , excited-state barriers, E_B , and energy, E_{CP} (in kJ mol^{-1}) at the crossing point of the T_a and T_s surfaces

Compound	E_D	E_B (S_a)	E_B (T_a)	E_B (T_s)	E_{CP}
Formaldehyde (1)	347 454 ^a	180 171 ^b	190 141 ^b 218 ^a	21 161 ^a 121 ^c	145
Acetaldehyde (2)					
C—H cleavage	373	235	253 65 ^d 245 ^c	34	186
C—CH ₃ cleavage	374	273	286 51 ^d 245 ^c	63	210
Acetone (3)	285	219	246	87	225
Di- <i>tert</i> -butyl ketone (4)	95	180	195	15	132
Acrolein (5)	373	222	225	124	189
Benzaldehyde (6)	402	246	244	219	

^a Ref. 24.^b Ref. 23.^c Ref. 25.^d Ref. 26.^e Ref. 27.

Table 3. Contributions (%) of reference (REF), singly (SC) and doubly (DC) excited configurations to ground- and excited-state wavefunctions of planar formaldehyde along the bitopic reaction path

		R_{CH_2} (pm)										
		100	110	120	140	150	160	170	180	200	250	300
S_0	REF	91.4	91.6	91.8	91.3	90.0	90.0	88.9	87.0	80.7	47.2	81.8
	SC	5.5	5.2	4.8	3.7	4.7	2.7	2.0	1.4	0.0	29.5	14.4
	DC	1.5	1.5	1.5	1.4	1.3	4.3	6.3	8.9	15.7	21.2	0.0
S_a	REF	96.5	96.3	95.8	94.1	92.8	78.4	75.0	72.0	69.0	78.6	90.0
	SC	1.1	1.2	1.2	1.2	2.9	16.4	19.3	21.2	24.5	14.4	4.3
	DC	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.1	1.7	2.1
T_a	REF	96.9	96.6	96.2	94.6	93.5	79.8	76.6	72.7	67.7	77.2	89.7
	SC	1.3	1.4	1.5	2.5	3.4	17.5	18.3	20.9	25.0	16.7	4.2
	DC	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.1	1.6	2.1
T_s	REF	98.5	98.3	91.9	91.1	90.5	94.8	95.0	95.1	95.4	95.6	95.6
	SC	0.0	0.0	1.8	3.3	4.4	0.0	0.0	0.0	0.0	0.0	0.0
	DC	0.0	0.0	0.0	0.0	0.0	0.0	1.0	1.1	1.1	1.2	1.3

geometry. In contrast to *ab initio* results,^{26,27} the activation energies for both α -cleavage reactions differ from each other, with the calculated barrier for the cleavage of the methyl group being higher. This is supported by at least some of the experimental data.^{16,17} SINDO1^{6a} and MINDO/3 calculations^{6b,c} also yield a higher barrier for the methyl cleavage, although the calculated values are much smaller because in these calculations the T_s state is calculated to be of $n\sigma^*$ character all along the reaction coordinate. This is in contrast to other theoretical results and experimental expectations,^{25,38} according to which the ${}^3\pi\pi^*$ state should be below the ${}^3n\sigma^*$ state in the equilibrium

geometry, so that the T_s state is of $\pi\pi^*$ nature in this geometry and becomes $n\sigma^*$ in nature only after the avoided crossing which is responsible for the barrier in T_s (see above).

In order to investigate the structural dependence of the α -cleavage reaction of saturated ketones, we extended the calculations to alkyl methyl ketones with the alkyl group varying from methyl in acetone (3) to *tert*-butyl. The results are shown in Figure 5 and indicate that the activation energy of the α -cleavage reaction depends only on the number of alkyl substituents at the α -carbon. With increasing degree of branching at the α -carbon, the T_1 barrier occurs earlier along the

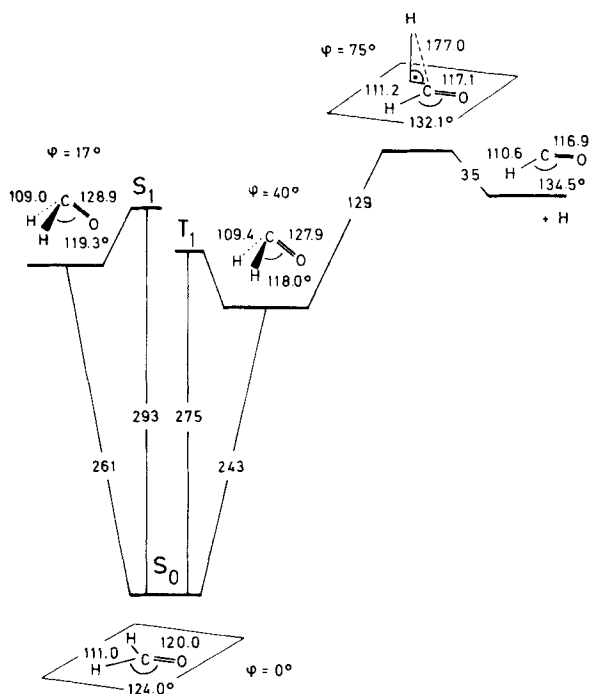


Figure 4. Optimized S_0 , S_1 and T_1 equilibrium and T_1 transition state and product geometries for the α -cleavage reaction of formaldehyde, and vertical and adiabatic excitation energies and activation energies on the T_1 surface

reaction coordinate and the activation energy decreases by ca 25 kJ mol⁻¹ for each alkyl substituent. The nature of the remaining alkyl substituent and branching in β -position of the leaving alkyl group have no influence on the activation energy, in very good agreement with experimental results.^{19,20}

DISCUSSION

The comparison of the MNDOC-CI results with

experimental data and with the *ab initio* results for acetaldehyde has shown that this method is well suited for a study of the mechanism of the photochemical α -cleavage reaction. From the potential energy surfaces in Figure 2a, it is seen that the photoreaction is expected to proceed in T_1 along the ditopic reaction path, and that an activation energy is required which stems from the barrier due to surface crossing which is avoided for non-planar geometries. This is in very good agreement with expectations from Salem correlation diagrams.³⁵ The existence of an activation barrier could even be predicted simply from the fact that the excitation is into the $n\pi^*$ configuration, whereas a $\sigma\sigma^*$ configuration is responsible for the bond breaking.³⁹ Hence simple correlations diagrams may be very useful, although they neglect the non-planarity of the system. According to the geometry optimization at the SCF level, the $n\pi^*$ excited states of ketones are calculated to be planar ($\varphi \leq 4^\circ$ for all molecules investigated), in contrast to the $n\pi^*$ states of aldehydes. During the reaction, the leaving group moves out of the carbonyl plane nearly at right-angles for both types of carbonyl compounds. The surface crossing is therefore avoided for all compounds considered. As the non-planarity is comparable for all reactions, the calculated barrier heights and positions are to a very good approximation proportional to the corresponding data obtained from the crossing point of the T_s and T_a surfaces for planar systems. This again emphasizes the usefulness of the correlation diagrams. Hence the fact that the barrier height and position are determined essentially by the degree of branching at the α -carbon of the bond which is going to be broken can be explained by assuming that the biradicaloid state $B_{\sigma\sigma}$ is stabilized if the alkyl radical is more stable, so that the crossing of correlation lines is shifted to shorter distances and thus corresponds to lower energies. This is exemplified by the calculated cross-sections for acetone (3) and di-*tert*-butyl ketone (4) show in Figure 6.

In unsaturated and aromatic ketones, on the other hand, the $\pi\pi^*$ state is stabilized by conjugation, which

Table 4. MNDOC results for bond distances (in pm) and angles (in degrees) of acetaldehyde in the equilibrium geometry (EQ) of S_0 and T_1 and in the T_1 transition-state geometries (TS) for H and CH_3 cleavage (*ab initio* values²⁶ in parentheses)

Parameter	S_0 (EQ)		T_1					
	EQ	(<i>ab initio</i>)	EQ	(<i>ab initio</i>)	TS_{CH_3}	(<i>ab initio</i>)	TS_{H}	(<i>ab initio</i>)
r_{CO}	120.5	(120.9)	128.7	(130.2)	118.0	(122.4)	118.1	(122.0)
r_{CC}	151.5	(150.7)	148.6	(150.8)	207.6	(213.4)	149.9	(152.9)
r_{CH}	111.6	(108.7)	109.8	(107.6)	111.2	(109.2)	167.5	(173.8)
r_{CH_m}	110.3	(108.4)	110.4	(108.4)	108.8	(107.4)	110.3	(108.4)
$\angle \text{OCC}$	125.4	(124.8)	122.4	(115.1)	122.8	(104.5)	137.2	(127.5)
$\angle \text{OCH}$	121.6	(120.9)	122.5	(112.2)	131.0	(125.0)	99.6	(98.8)
$\angle \text{H}_m\text{CC}$	110.8	(109.9)	115.7	(110.5)	102.8	(110.7)	110.1	(109.6)
φ	0.0	(0.0)	12.1	(41.2)	67.1	(76.7)	60.3	(72.2)
τ	0.0	(0.0)	49.6	(53.2)	-1.0	(58.5)	0.0	(38.4)

Table 5. Geometries (angles in degrees) and energy changes (in kJ mol^{-1}) along the T_1 minimum energy path for the α -cleavage reaction of acetaldehyde

Cleavage	Parameter	ΔR (pm)						
		0	10	30	50	58	90	190
H cleavage (ΔR_{CH})	$\angle OCC$	125.4	123.7	129.8	135.9	137.2	138.9	140.2
	φ^a	12.2	25.0	46.2	60.3	60.3	—	—
	ΔE_{CI}^b	—	12.6	84.8	125.8	131.0	127.6	104.5
	ΔE_{SCF}^b	—	17.1	89.9	137.1	138.3	112.9	89.9
	$\Delta \Delta E_{opt}^{b,c}$	—	-1.3	17.6	30.5	—	22.6	24.7
CH ₃ cleavage (ΔR_{CC})	$\angle OCH$	121.6	117.0	122.6	130.1	131.0	135.0	135.1
	φ^a	12.2	25.7	46.3	65.5	67.1	—	—
	ΔE_{CI}^b	—	14.1	88.5	140.5	146.8	145.5	111.9
	ΔE_{SCF}^b	—	18.9	103.2	149.6	152.5	130.8	93.6
	$\Delta \Delta E_{opt}^{b,c}$	—	-3.3	7.9	52.3	—	25.1	38.9

^a $\varphi = \angle OCRX - 180^\circ$, where $\angle OCRX$ is the dihedral angle between the leaving group X and the acyl fragment.

^b Energies relative to the energy at equilibrium geometry.

^c $\Delta \Delta E_{opt} = \Delta E_{SCF}(\text{not opt.}) - \Delta E_{SCF}(\text{opt.})$ gives an estimate of the influence of geometry optimization on SCF energies.

at first sight should again shift the crossing point towards an earlier and therefore smaller activation barrier. However, our results show that, in agreement with experimental data, the activation energy E_a is more or less constant or even higher if the π system is as large as in, e.g., *p*-phenylbenzaldehyde. Figure 2 shows that

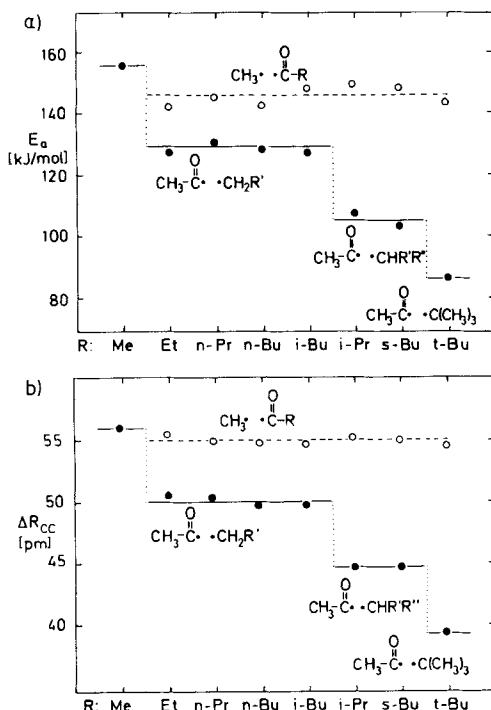


Figure 5. (a) MNDOC-SCF activation energies and (b) differences ΔR between the C—X distances in T_1 transition states and T_1 equilibrium geometries for the α -cleavage of the methyl (○) and the alkyl (●) group of alkyl methyl ketones

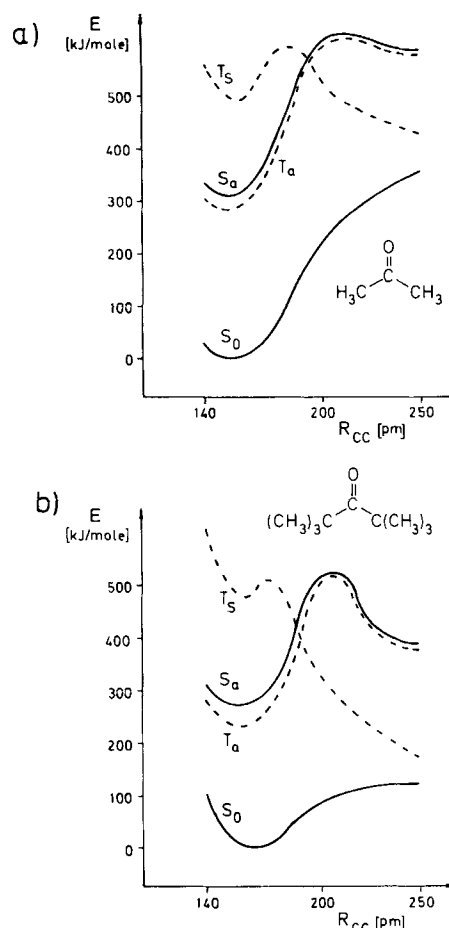


Figure 6. Cross-section through the potential energy surfaces of (a) acetone and (b) di-*tert*-butyl ketone along the ditopic reaction path for the planar α -cleavage reaction

this is due to the fact that there is a barrier in the T_s state, the origin of which can be explained by the natural correlation of both the $^3\pi\pi^*$ state of the educt and the $^3B_{\sigma\sigma}$ state of the product with high lying excited states. Hence the crossing point between the T_s and T_a states is not determined primarily by the energy of T_s at the educt geometry, but rather by the energy and the position of this barrier in T_s . If T_s is stabilized to such an extent that it is below T_a all the way along the reaction coordinate, the activation energy is determined by this T_s barrier and may therefore become larger than in the case where it is determined by the crossing between T_s and T_a . The barrier in T_s also explains why a change of reference configuration occurs along the reaction coordinate (cf. Table 3), which is not to be expected from a Salem correlation diagram.

In conclusion, we may say that for a discussion of photochemical reactions correlation diagrams and quantum chemical calculations are complementary insofar as correlation diagrams cannot be drawn properly without the information about state energies and barrier positions which can be obtained only from calculations, whereas quantum chemical calculations can be performed much more effectively if correlation diagrams are used in order to establish where to look for interesting parts of the potential energy surfaces.

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