Quantum-chemical study of the properties of the excited states of organic molecules
V. Excited states and photolytic dissociation of formaldehyde

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Dedicated to Academician V. Kellö, in honour of his 65th birthday

A semiempirical quantum-chemical MINDO/2 method has been tested for description of the dissociation curves of the CH bond in formaldehyde in its ground and excited singlet and triplet states. A Fock operator of Nesbet's type was used in the SCF procedure; the consequent configuration interaction contained monoexcited and some selected biexcited configurations necessary for correct description of the dissociation. Irrespective of some shortcomings of MINDO/2 parametrization for describing excited states it seems to be suitable for qualitative conclusions on the mechanism of photolytic decomposition of organic ketones.

Полуэмпирический квантово-химический MINDO/2 метод был использован с целью проверить его пригодность для описания кривых диссоциации CH связи в молекуле формальдегида в основном, в возбужденном синглетном и триплетном состояниях. Для SCF расчетов был использован оператор Фока типа Несбета. В последующих расчетах по методу взаимодействия конфигураций были включены однократно возбужденные и выбранные двухкратновозбужденные конфигурации необходимы для качественно правильного описания диссоциации. Было показано, что MINDO/2 параметризация, несмотря на некоторые ее недостатки, пригодна для качественного обсуждения механизма фотолитического распада органических кетонов.

With regard to its simple structure and significance in industrial chemistry and in atmospheric processes, formaldehyde has been intensively experimentally and theoretically investigated. Detailed knowledge of photochemical processes in formaldehyde is not only of theoretical importance but is also valuable for studying formation of the smog in towns, where formaldehyde is one of the main components [1, 2].

The electronic spectrum of formaldehyde has been thoroughly analyzed [3]. The main sequence of absorption bands between 353 and 230 nm corresponds to the symmetrically forbidden $n \rightarrow \pi^*$ ($^1A'$) transition and is accompanied by weak absorption in the region between 396.7 and 360 nm belonging to symmetrically and spin-forbidden transition $^3A_2 \leftarrow {}^1A_1$. All the other absorption bands are ascribed [3] to Rydberg transitions to orbitals with the principal quantum number 3 and higher as has also been confirmed by nonempirical calculations of *Peyerimhoff et al.* [4]. Photolysis of formaldehyde proceeds by three primary reactions [5].

$$H_2CO \xrightarrow{h\nu} H_2 + CO \qquad (A)$$

$$H_2CO \xrightarrow{h\nu} H^\bullet + HCO^\bullet \qquad (B)$$

$$H_2CO \xrightarrow{h\nu} 2H^\bullet + CO \qquad (C)$$

The process (A) dominates at large wavelengths ($\lambda > 355$ nm). The reaction (B) proceeds at wavelengths below 313 nm exclusively, the reaction (C) occurring at 130—180 nm. The final photolysis products are H_2 and CO.

Calculations

Calculations of transition energies were done in semiempirical MINDO/2, INDO, and CNDO/S parametrizations basing on the ground state SCF orbitals and using configuration interaction with 16 lowest monoexcited configurations.

An HF operator of Nesbet's type [6] in MINDO/2 parametrization in the form

$$\hat{F} = \hat{h} + \sum_i (2\hat{J}_i - \hat{K}_i) - (\hat{J}_a - \frac{1}{2}\hat{K}_a) + (\hat{J}_b - \frac{1}{2}\hat{K}_b) \qquad (1)$$

was used for calculating energy of excited $\varphi_a \rightarrow \varphi_b$ configuration along the reaction pathway. Index i in eqn (*1*) passes through doubly occupied molecular orbitals in the ground state, a, b are indices for orbitals participating in excitation $\varphi_a \rightarrow \varphi_b$. We at first modelled dissociation of formaldehyde removing hydrogen atom from carbon in the molecular plane, *i.e.* maintaining the C_s symmetry, and at constant values of other internal coordinates of a molecule. The starting geometry corresponded to the experimental geometry of formaldehyde in the ground state

$$R_{CO} = 1.21 \times 10^{-10}\ \text{m} \qquad R_{CH} = 1.1 \times 10^{-10}\ \text{m}$$

and $\sphericalangle HCH = 121.1°$.

As is known from the experiments [3] and as has been shown in the calculation of optimalized geometry in Part II of this series [7], formaldehyde assumes pyramidal structure in the excited state. Therefore the model of planar dissociation is only a rough approximation.

The second reaction pathway starts from the bent pyramidal structure of formaldehyde in experimental geometry of the excited $^1A''$ state [3] ($R_{CH} = 1.09 \times 10^{-10}$ m; $R_{CO} = 1.32 \times 10^{-10}$ m; $\sphericalangle HCH = 119°$ and the out of HCH plane angle of the CO bond is 31°) and the CH bond breaking takes place in the direction of the bond. The fundamental difference between this and the previous case is that the system studied has no symmetry along the reaction path and thus the orbitals and states having the same multiplicity can only be classified according to their energies. All state crossings with the same multiplicity vanish consequently.

The SCF calculation was done for a monoexcited configuration corresponding to the excitation between frontier orbitals. Similarly to the planar model, a configuration with closed shells, four lowest paired biexcited and nine lowest monoexcited configurations were included into CI.

Results and discussion

Let us first note the Franck—Condon transition energies of a formaldehyde molecule. Table 1 contains values of the transition energies calculated with a complete monoexcited CI from SCF MO's of the ground state in various semiempirical methods. For the comparison purposes, we also present *ab initio* CI data reported by *Buenker* and *Peyerimhoff* [8] calculated in DZ bases set. As has

Table 1

Transition energies for formaldehyde (E/eV)

Excited state	MINDO/2 CI—S*	INDO CI—S	CNDO/S CI—S	*ab initio* [8] CI	exp [3]
$^1A_2(n\rightarrow\pi^*)$	2.03	4.65	3.17	3.43	3.5 —5.39
$^1B_1(\sigma\rightarrow\pi^*)$	4.43	9.14	8.32	8.16	
$^1B_2(n\rightarrow\sigma^*)$	4.73	10.42	9.23	10.44	
$^1A_1(\pi\rightarrow\pi^*)$	6.65	11.82	9.50	12.13	
$^3A_2(n\rightarrow\pi^*)$	1.56	4.09	3.17	3.01	3.12—3.44
$^3A_1(\pi\rightarrow\pi^*)$	3.27	7.21	5.28	4.99	
$^3B_1(\sigma\rightarrow\pi^*)$	3.47	8.32	8.23	7.62	
$^3B_2(n\rightarrow\sigma^*)$	3.68	8.08	8.32	9.95	

* CI—S — configuration interaction between singly excited configurations.

already been mentioned, only the values for $^{1,3}n \rightarrow \pi^*$ transitions are known from experimental measurements. It is interesting to note that the order of eight values of transition energies for singlet and triplet excitations between valence orbitals computed by semiempirical methods is almost the same as the order calculated by nonempirical methods. Similarly as for the studied molecules in Part III of this series [9], the calculated MINDO/2—CI transition energies are systematically too low (Table 1).

We have already described a calculation of the energy of the $^{1,3}A''(n \rightarrow \pi^*)$ and $^{1,3}A'(n \rightarrow \sigma^*)$ configurations at the SCF level along the reaction path. For the excited $A'(\pi \rightarrow \pi^*)$ configuration, the SCF procedure converges only at the starting geometry and at large C—H distances, $R_{CH} > 2.58 \times 10^{-10}$ m. At smaller C—H distances, the orbital symmetry was usually disturbed and collapse on an energetically lower A' configuration of $(n \rightarrow \sigma^*)$ type occurred. The $A'(\pi \rightarrow \pi^*)$

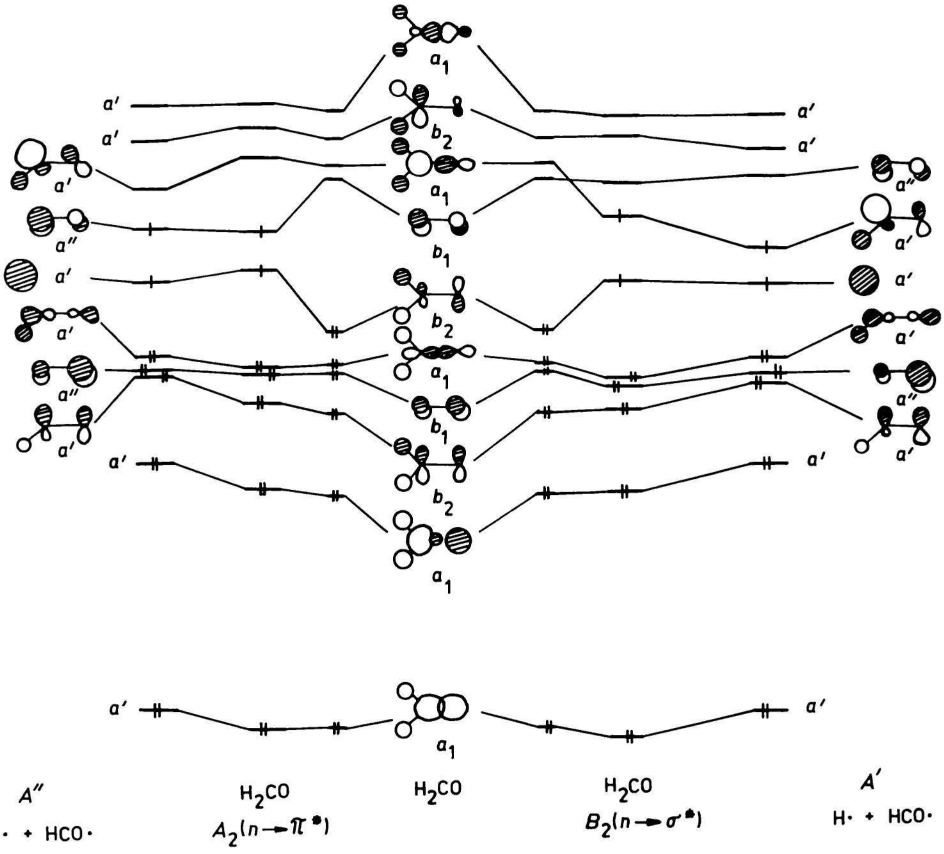

Fig. 1. Orbital correlation diagram for dissociation $H_2CO \rightarrow H^\bullet + HCO^\bullet$. Left for $n \rightarrow \pi^*$ (A_2) state, right for $n \rightarrow \sigma^*$ (B_2) state.

configuration cannot obviously lead to radical products of dissociation because both singly occupied orbitals π and π^* remain localized on the HCO fragment. Fig. 1 shows the orbital correlation diagram for planar formaldehyde dissociation to the A' and A'' states. The originally nonbonding $2b_2$ orbital predominantly localized on oxygen atom passes during dissociation to $1s$ orbital of the removing hydrogen atom in both studied pathways.

The excited $n \rightarrow \sigma^*$ configuration gives rise to σ formyl radical and to a hydrogen atom, *i.e.* to products in the ground state; when π^* orbital is occupied in $n \rightarrow \pi^*$ configuration, the π formyl radical is formed (Fig. 1).

Fig. 1 shows that changes in orbital shapes dependent on the configuration for which they were calculated are not striking. If we look at $\sigma^*(6a')$ and $\pi^*(2a'')$ orbitals in $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ configurations, we can see that their character varies only slightly, not taking into account whether the respective orbital has been occupied or not during calculation. This is so because of minimal basis set used and thus the orbitals are little flexible. *Ab initio* calculations on formaldehyde photodissociation done by *Fink* [10] with AO basis set including diffusion functions with the principal quantum number 3 located on CO bond revealed, however, a remarkable changes in character of the $2b_1$ orbital depending on the fact whether the orbital was occupied or not. When the orbital was not occupied, it was of Rydberg character, when it was occupied, it was purely valence in character.

Fig. 2 shows dissociation curves for the excited configurations of $^{1,3}A''$ and $^{1,3}A'$ states obtained from separate SCF calculations. The energies for dissociation curve

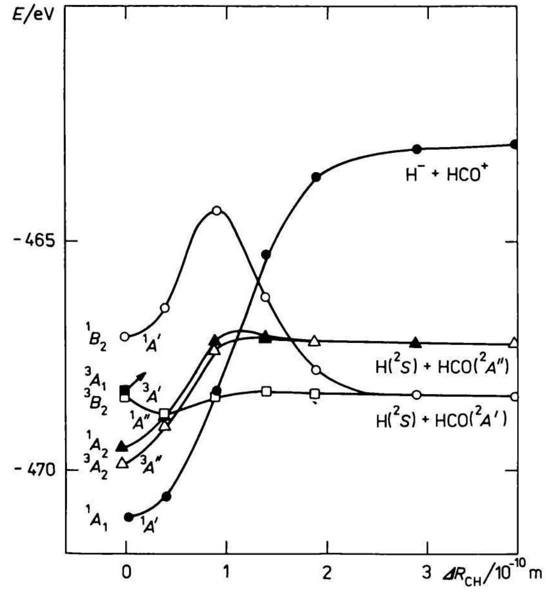

Fig. 2. Curves of the SCF energy for planar dissociation $H_2CO \rightarrow H\bullet + HCO\bullet$ in various electron configurations (for details see the text).

of the ground state configuration ${}^1A'$ were calculated from SCF orbitals of either $A'(n \rightarrow \sigma^*)$ or $A''(n \rightarrow \pi^*)$ excited configurations depending on which energy of the ground state configuration calculated in this way is lower. The curves show that in planar dissociation the first excited singlet and triplet states (${}^{1,3}A_2$) dissociate into products of the reaction (C) in the excited state, *i.e.* into HCO π radical; the course of the singlet and triplet states is very similar and has a little maximum in the region $\Delta R_{CH} \approx 1 \times 10^{-10}$ m. The source of radical products in the ground state is the excited ${}^3A'({}^3B_2)$ triplet showing a distinct dissociation curve with a little maximum also in the region $\Delta R_{CH} \approx 1 \times 10^{-10}$ m. The respective singlet ${}^1A'$ state in this range passes through a significant barrier. Its origin is in a sudden increase of the value of an exchange integral between singly occupied orbitals. The orbital b_2 (Fig. 1), originally nonbonding, is in formaldehyde localized predominantly on oxygen and a_1, originally antibonding orbital, is localized on carbon. The shift of electron density from the originally nonbonding orbital in the direction to hydrogen atom in the region of $\Delta R_{CH} \approx 1 \times 10^{-10}$ m causes that local overlap of these orbitals is here maximal. This results in a rapid increase of exchange integral and thus also of the corresponding singlet-triplet splitting. The following course ($\Delta R > 1 \times 10^{-10}$ m) of the dissociation curve of the excited configuration of ${}^1A'$ to a common dissociation limit with ${}^3A'$ cannot be qualitatively correct; it crosses the respective curve for the ground state configuration having the same symmetry, *i.e.* ${}^1A'$ and thus the two configurations strongly interact in the crossing region giving rise to avoided crossing.

The dissociation curve which should describe the ground state (${}^1A'$) energy leads necessarily to products in the ground state while the curve for the first excited state of ${}^1A'$ symmetry yields products in the excited states. The one-configurational function thus cannot properly define avoided crossing of such configurations. Fig. 3 shows dissociation curves after configuration interaction including 14 configurations, namely: a configuration corresponding to the closed-shell ground state, nine configurations monoexcited with respect to the former, and four paired biexcited configurations. SCF molecular orbitals for the configurations were obtained from the starting monoexcited ($n \rightarrow \pi^*$) configuration with A' symmetry. After CI, the lowest singlet and the lowest triplet (${}^{1,3}A'$) states have a common dissociation limit and yield products in their ground states. Dissociation curves of ${}^{1,3}A''$ states did not significantly change with respect to one-configurational description because in the CI function for this state the same configuration remains predominant during dissociation.

According to the increasing energy ion fragments HCO^+ and H^- (Fig. 3) become products. Basing on "chemical" experience the dissociation into H^+ and HCO^- seems to be more favourable. The theoretical result obtained might be considered a shortcoming of the MINDO/2 parametrization overstabilizing atomic orbital on hydrogen compared with the respective MO on HCO. However, the *ab initio* SCF

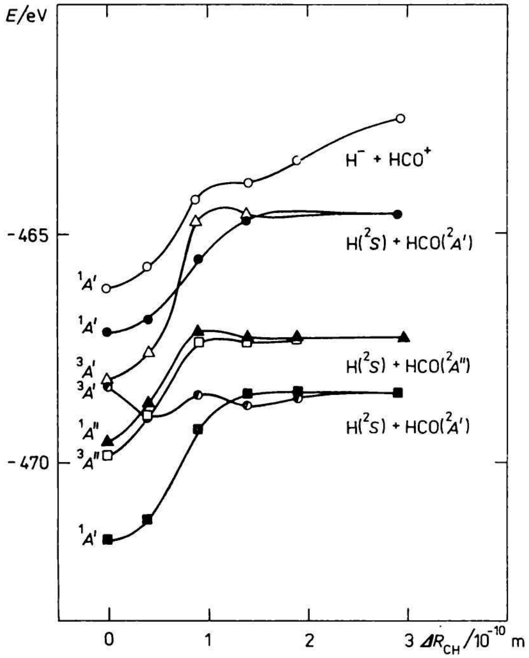

Fig. 3. Curves of CI energy for planar dissociation $H_2CO \rightarrow H^\bullet + HCO^\bullet$ in various electron states (for details see the text).

calculation in 4—31 G basis set confirmed that the system $H^- + HCO^+$ has lower energy (by 46 eV) than the $H^+ + HCO^-$ system (Table 2). Ionic products are of no interest from the photochemical point of view; because of their high energy, they cannot be regarded as primary photolysis products. If we model reaction pathway by the dissociation of pyramidal form, the lowest triplet state has a common dissociation limit with the ground state, *i.e.* it dissociates adiabatically to ground state products (Fig. 4). The calculated value for the CH bond energy in formaldehyde, 383.5 kJ mol^{-1}, agrees well with the experimental value, *i.e.* 360 kJ mol^{-1} [11]. The energy difference between the ground state and the first excited state of

Table 2

Energies of ion fragments of formaldehyde (E/eV)

	$HCO^{-a} + H^+$	$HCO^{+b} + H^-$
MINDO/2	− 454.598	− 460.269
4-31 G	−3034.157	−3080.199

$R_{CH} = 1.085 \times 10^{-10}$ m; $R_{CO} = 1.130 \times 10^{-10}$ m.
a) ∢HCO = 120°; *b*) ∢HCO = 180°.

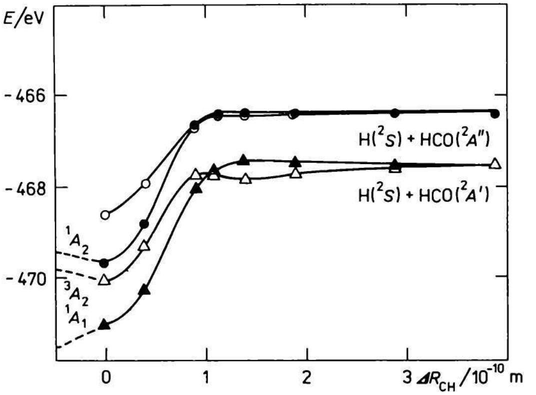

Fig. 4. Curves of CI energy for pyramidal dissociation $H_2CO \rightarrow H^\bullet + HCO^\bullet$ in various electron states (for details see the text).

the HCO radical − 1.17 eV is also close to the experimental value of 1.15 eV [3]. The triplet states indicate a low maximum at CH bond lengthening by about 1×10^{-10} m while the singlet states have smooth dissociation curves. Their shape is consistent with that of curves computed by *Fink* [10].

During formaldehyde photolysis in the long-wave region ($\lambda > 350$ nm), the first excited singlet state ($^1A_2$) is most populated. This state leads by intersystem crossing probably to the lowest triplet state ($^3A_2$), which, along its "own" hypersurface, dissociates into the ground state products. But a transition from the excited singlet state to the potential hypersurface of the ground state in some of its higher vibration states with consequent dissociation into the same products is also possible. At lower wavelength values, the photolysis into the excited state of HCO radical is possible, which is accompanied by the emission due to radiational transition to its ground state.

Although the MINDO/2 method cannot reliably provide the energy of the excited states, dissociation curves obtained are useful for qualitative discussion on dissociation in the ground and excited states. Our approach is applicable to a study of the influence of the electron structure on photolytic dissociation of larger organic ketones, where the use of *ab initio* methods is limited by computation technique.

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