
**QUANTUM CHEMICAL MODELLING OF THE REACTIONS
PARTICIPATING IN HYDROCARBON COMBUSTION.
PRODUCTION OF THE H ATOMS**

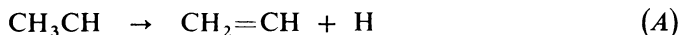
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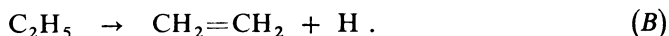
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The dissociation reactions giving rise to the H atoms from methylcarbene and ethyl radical have been studied on the *ab initio* and MINDO/3 methodical level. On the basis of the transition state theory, the temperature dependence of rate constant has been calculated by using the harmonic oscillator-rigid rotor approximation. The results which indicate equal rate of the course of both reactions are compared with available experimental data.

Owing to their reactivity, carbenes are a topic of many theoretical papers¹⁻⁴. They are supposed to participate also in hydrocarbon combustion⁵. In the scheme proposed by Bakoš and Rychlý⁶⁻⁷, carbenes represent the reactive intermediates on the basis of which the mechanism of polymer combustion is proposed. In contrast to the radical mechanism of hydrocarbon oxidation implying the peroxide and alkyl radicals, the authors put forward a scheme where the reaction of oxygen with hydrocarbon yielding hydrogen peroxide and the corresponding carbene appears to be the fundamental initiating reaction. One of the reactions of this scheme is also the formation of atomic hydrogen which arises from carbenes to give unsaturated hydrocarbons. We use the elimination of atomic hydrogen from methylcarbene



as a model for investigating this reaction. The temperature dependence of reaction rate is studied on the basis of the transition state theory⁸. The β -elimination of the hydrogen atom from radicals appearing in the peroxide scheme of hydrocarbon combustion is regarded as reference reaction. This reaction has been modelled by the decomposition of ethyl radical



Though this second reaction was the topic of several theoretical studies⁹⁻¹⁵, the reaction concerning the cleavage of the C—H bond in compounds of the methyl-

carbene type has not been, according to our knowledge, theoretically studied yet. The aim of this study is to compare the rate constants of both reactions, especially in the temperature range which is referable to the region corresponding to hydrocarbon combustion.

METHODS AND CALCULATION

It is known at present that the study of energetic hypersurfaces of greater systems offers the problem to select the most suited quantum chemical method. If we want to carry out a full optimization of geometrical parameters, we are limited to small bases in the *ab initio* method or we must use semiempirical methods. As for the selection in the *ab initio* method, it appears that the most effective approach is to find stationary points in the STO-3G basis and to determine the energetic differences between them by the single-point calculation in the 4-31G basis¹⁶. Among the semiempirical methods, the MINDO/3 method which was parametrized mainly for these purposes is most frequently used. For this reason, we have used either approach in this paper. As the UHF wave function qualitatively correctly describes the dissociation limits of molecules, we used the UHF approach for the description of dissociation processes *A* and *B* on both levels. The geometry along the reaction path was determined by gradual optimization of internal coordinates in the minimal STO-3G basis. For the evaluation of activation barriers, we used the 4-31G basis in minima and saddle points determined by the above optimization. The *ab initio* calculations were performed by means of the programme GAUSSIAN-70 (see¹⁷). The programme GEOMO/RV (see¹⁸) was used to the UHF MINDO/3 calculations. The programme also contains the gradient method of optimization of internal coordinates which was used in this case. The frequencies of normal vibrational modes as well as the moments of inertia were obtained by the Schmidling method¹⁹ which is built in the programme GEOMO/RV. These data were also used in combination with the 4-31G results of the calculation of energetic barriers.

REACTION PATH BY THE *ab initio* METHOD

For the reaction giving rise to vinyl radical by elimination of the hydrogen atom, we have started from the known fact that the hydrogen atom is eliminated from the methyl group of the triplet carbene²⁰. The reaction pathway was modelled by the variation in distance of the eliminated hydrogen (in Fig. 1a denoted r_1). The optimized geometry of methylcarbene and vinyl radical for the minimal STO-3G basis was taken from literature²¹. In the staggered conformation of methylcarbene which was only slightly more stable (~ 1 kJ/mol) than the eclipsed one, the hydrogen in the methyl group was fixed in the direction of elimination. The angle α was not optimized. Its variation with respect to the angle α in vinyl radical was 4.4° . The geometry in particular points of the reaction pathway was optimized by successive optimization of individual geometrical parameters. Their values and energies corresponding to particular points are given in Table I. The changes in r_3 , r_4 , and r_5 which are of order of 10^{-13} m are not given and the angle α is 126.4° for methylcarbene and 130.8° for vinyl radical. The angle δ is dihedral for hydrogen between r_5 and r_3 bonds. The maximum energy was found at the distance $r_1 = 2.50 \cdot 10^{-10}$ m with the barrier of 218.1 kJ/mol. This value was modified for the calculation of rate constants

by means of the zero-point energy (ZPE) correction calculated from the MINDO/3 frequencies. This correction was -27.7 kJ/mol. Thus the result of calculation of this part of investigation is the value of 190.4 kJ/mol found for the activation barrier of reaction *A*. This value will be used for the calculation of rate constants. The experimental measurements of activation energy for dissociation of the hydrogen atom from ethyl radical gave the value of 171.1 ± 2 kJ/mol (see²²). The study of the opposite reaction giving rise to ethyl radical supplied data about the activated com-

TABLE I
Ab initio results^a for reaction *A*

r_1	r_2	β	γ	δ	$E_{\text{STO-3G}}$	$E_{4-31\text{G}}$
1.089	1.509	110.6	111.3	58.0	-202 431.4	-204 607.9
1.5	1.490	110.6	111.3	50.2	-202 231.0	
2.0	1.470	115.9	116.6	39.3	-202 079.9	
2.3	1.445	116.6	117.3	32.2	-202 065.7	
2.4	1.412	116.7	117.5	30.7	-202 064.1	
2.5	1.410	116.8	117.6	29.4	-202 063.2	-204 389.8
2.6	1.390	117.3	118.4	26.1	-202 065.4	
2.7	1.385	119.8	120.5	14.0	-202 065.5	
∞	1.357	121.4	122.3		-202 181.1	-204 417.1

^a Lengths in multiples of 10^{-10} m, angles in degrees, energies in kJ/mol.

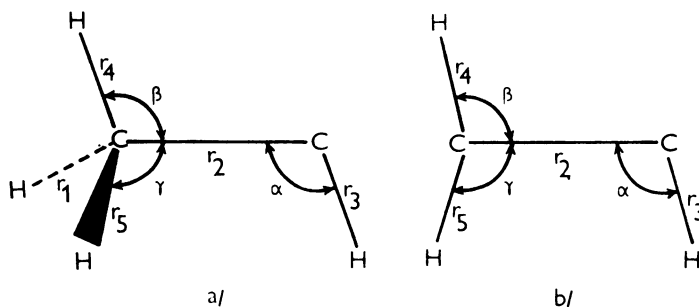


FIG. 1
Geometry of methylcarbene (*a*) and vinyl radical (*b*)

plex through which the reaction proceeds in both directions. Nomura and Iwata¹² allege that the distance of the dissociated hydrogen is $1.8 \cdot 10^{-10}$ m while Hase and coworkers¹⁵ quote $2.0 \cdot 10^{-10}$ m. Kato and Morokuma²³ obtained the energetic maximum at the distance of $2.03 \cdot 10^{-10}$ m whereas Nagase and Kern²⁴ found the value of $2.015 \cdot 10^{-10}$ m. The value obtained by us in the minimal basis is $1.8 \cdot 10^{-10}$. The procedure of searching for the energetic maximum was analogous to that used for reaction (A). The hydrogen of the methyl group was fixed in the direction of elimination while the individual geometrical parameters were successively optimized. The geometry of the saddle point as well as the values of parameters is represented in Fig. 2. The energetic difference corresponding to this geometry is 207.2 kJ/mol for the 4-31G basis which gives the value of 186.1 kJ/mol after ZPE correction.

REACTION PATH BY THE MINDO/3 METHOD

In this case, the reaction pathway of the formation of vinyl radical was modelled by the variation in distance of the eliminated hydrogen like r_1 in the *ab initio* calculations (Fig. 1). Its direction was not, however, fixed as far as to the distance of $1.9 \cdot 10^{-10}$ m. In this point, there is the barrier of hydrogen migration into the region of the second carbon atom. Further variation was performed by fixing the hydrogen in the direction to which the angles of the distance of $1.9 \cdot 10^{-10}$ m corresponded. Table II contains the values of some geometrical parameters and energies for particular points of the reaction pathway. The maximum energy was found in the distance of $2.6 \cdot 10^{-10}$ m, its value being 237.4 kJ/mol. After ZPE correction of this value we obtained 209.7 kJ/mol.

The energy differences between the values corresponding to $2.3 \cdot 10^{-10}$ m and $2.6 \cdot 10^{-10}$ m are very small and for this reason, we used the variation in distance of $0.1 \cdot 10^{-10}$ m.

We used analogous procedure for studying reaction (B). The direction of elimination of the dissociated hydrogen was not fixed as far as to the distance $r_1 = 1.7 \cdot 10^{-10}$ m. From this distance the direction was determined by the bond angle $\alpha = 89.7^\circ$. The obtained values of geometrical parameters for the transition state are presented in Fig. 3. The value of activation energy for this reaction is 224.0 kJ/mol. However, it is only 202.9 kJ/mol after the ZPE correction.

If we compare the values obtained by the *ab initio* method and by the MINDO/3 method, we can see that both methods give lower barriers for the dissociation of ethyl radical, *i.e.* by 4.3 and 6.8 kJ/mol respectively. We shall show later that the activation energies obtained by the *ab initio* method are slightly overestimated which means that the results obtained by the MINDO/3 method should show still greater deviations from experimental values. Therefore we are going to use only the values of activation barriers obtained by the *ab initio* method.

RATE CONSTANTS

The absolute values of the rate constants of unimolecular reactions are usually calculated on the basis of the RRKM theory^{25,26}. However, at normal pressure the difference between the rate constants obtained according to the RRKM theory^{25,27} and the transition state theory (TST) assumes the values which are negligible from the view-point of our aim (comparison of the rate constants of reactions) (A) and (B). For this reason, we could use the TST theory for calculating the absolute values

TABLE II
MINDO/3 results for reaction A

r_1	r_2	α	β	γ	δ	ε^a	ζ	E
1.113	1.4	142.0	113.0	112.0	60.0		300.0	-29 967.4
1.3	1.394	145.0	116.0	115.6	48.6	108.7	292.3	-29 920.3
1.7	1.319	144.4	123.0	122.5	7.9	97.8	273.0	-29 781.5
1.9	1.303	145.3	125.0	123.6	1.6	94.1	270.0	-29 754.0
2.1	1.297	145.6	125.0	123.7	0.			-29 739.7
2.3	1.294	145.9	125.1	123.7	0.			-29 733.0
2.5	1.292	145.9	125.1	123.8				-29 729.6
2.7	1.291	145.9	125.2	123.8				-29 730.3
∞	1.291	146.3	125.2	123.9	0.			-29 731.9

^a ε is the bond angle HCC for the eliminated hydrogen and ζ is its dihedral angle.

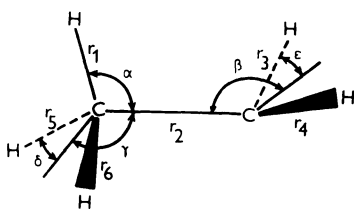


FIG. 2

Geometry of $\text{H}\cdots\text{C}_2\text{H}_4$ in the saddle point
 $r_1 = 1.9 \cdot 10^{-10}$ m, $r_2 = 1.386 \cdot 10^{-10}$ m,
 $r_3 = r_4 = r_5 = r_6 = 1.082 \cdot 10^{-10}$ m, $\alpha =$
 $= 111.4^\circ$, $\beta = 206.7^\circ$, $\gamma = 177^\circ$, $\varepsilon = 58.4^\circ$,
 $\delta = 58.2^\circ$

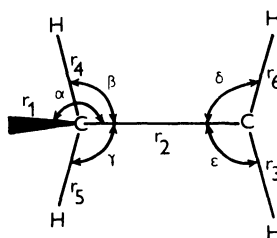


FIG. 3

Geometry of the saddle point $\text{H}\cdots\text{C}_2\text{H}_4$
 $r_1 = 2.5 \cdot 10^{-10}$ m, $r_2 = 1.315 \cdot 10^{-10}$ m,
 $r_3 = r_4 = r_5 = r_6 = 1.099 \cdot 10^{-10}$ m, $\alpha =$
 $= 89.7^\circ$, $\beta = \gamma = \delta = \varepsilon = 124.6^\circ$, hydrogens
 1° over the plane

of rate constants. This theory is based on the equation

$$k = l \frac{k_B T}{h} \frac{Q^\ddagger}{Q_{re}} \exp(-\Delta H_0^\ddagger / RT) \quad (1)$$

where Q_{re} and Q^\ddagger are partition functions of the reactant and activated complex, ΔH_0^\ddagger is the activation enthalpy at the absolute zero temperature, and l is a statistical

TABLE III

Summary of results for reactions *A* and *B*

	Reaction <i>A</i>		Reaction <i>B</i>	
	calculation		calculation	experiment ^a
Zero point correction (kJ/mol)	27.7		21.1	
ΔH_0^\ddagger (kJ/mol)	190.4		186.1	
E_a (kJ/mol)	198.3		191.3	171.1
$\log A$ (s^{-1})	14.9		14.4	14.4
k (s^{-1})	$7.9 \cdot 10^{14} e^{-198.3/RT}$		$2.7 \cdot 10^{14} e^{-191.3/RT}$	$2.7 \cdot 10^{14} e^{-171.1/RT}$

^a See ref.²⁹.

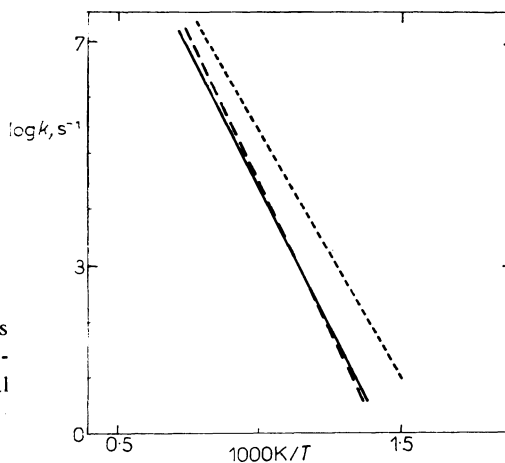


FIG. 4

Temperature dependence of rate constants of dissociations of: *a* methylcarbene (reaction *A*), ---- calculated, *b* ethyl radical (reaction *B*), experimental, ——— calculated

factor²⁸ (in either case it was assumed $l = 6$). The influence of the tunneling can be neglected at the temperatures of combustion (above 500 K).

We used the geometry determined by the MINDO/3 optimization for constructing the partition functions in the rigid rotor-harmonic oscillator approximation. The vibrational frequencies were calculated from the force constants obtained by the MINDO/3 method and applied to the calculation of the ZPE correction E_0 . The activation barriers resulting from the *ab initio* calculation in the 4-31 basis were used.

The temperature dependence of $\log k$ determined from equation (1) is represented in Fig. 4 and the final summarization is given in Table 3. The comparison with the experimental temperature dependence found for the dissociation of ethyl radical²⁹ shows that the values of the calculated rate constants are underestimated approximately by one order. Because of a great number of approximations which are involved in our procedure, we may admit that it is an acceptable agreement with experiments which justifies us to use this combined procedure for relative comparison of the rate constants of chemical reaction. The deviation from experiment is mainly due to the overestimation of the activation energy E_a by 19.8 kJ/mol (Table III). In order to eliminate this deviation, we ought to use quite greater basis sets and more exact methods comprising the correlation energy which would put much greater demands for calculation.

A comparison of the rate constants of both reactions, *i.e.* elimination of the H atom from methylcarbene (A) and from ethyl radical (B) leads to some conclusions. First of all, it is evident that the rate constants of both reactions are practically equal in the investigated temperature range 700–1 200 K. The dissociation of ethyl radical slightly prevails at lower temperatures but the dissociation of methylcarbene begins to come forward with increasing temperature. This fact may be explained on the basis of a greater preexponential factor A and activation barrier ΔH_0^\ddagger for the reaction of methylcarbene. It means from the view-point of mechanisms of hydrocarbon combustion that, besides radicals, carbenes can be an equally good source for the generation of the H atoms. Provided the concentration of radicals and carbenes is equal, the H atoms originated from the cleavage of the C—H bond in β -position with respect to the carbene centre will slightly prevail with increasing temperature.

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