# QUANTUM CHEMICAL MODELLING OF REACTIONS IN HYDROCARBON COMBUSTION. STUDY OF THE $CH_4 + O_2$ REACTIONS

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The rate constants of two alternative reactions, *i.e.* $CH_4 + O_2 \rightarrow CH_2 + H_2O_2$ and $CH_4 + O_2 \rightarrow CH_3 + HOO$ have been studied by the *ab initio* and MINDO/3 methods. A preliminary appreciation of the used methods has been done with a selected set of carbene reactions. The characteristics of minima as well as the saddle points on the corresponding reaction paths of both reactions have been found. The discussion of the relative probability of a pathway of the above-mentioned reactions is based on the rate constants determined by the use of transition state theory.

The interactions of alkanes with molecular oxygen and subsequent oxidation reactions are processes which are of outstanding importance in various fields of chemistry and biology. One of these fields is the study of combustion of polymers. Besides the classical mechanism of combustion based on the hydroperoxide and alkyl radicals a reaction scheme was put forward recently where carbenes functioned as reactive particles[1,2]. The major problem of this hypothetical scheme is the initiation reaction giving rise to carbenes. One of the possible reactions of this type is a direct interaction between hydrocarbon chain and $O_2$ which proceeds with the simplest alkene, *i.e.* $CH_4$ as follows

$$CH_4 + O_2 \rightarrow CH_2 + H_2O_2 \qquad (A)$$
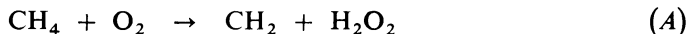
in competition with the radical reaction

$$CH_4 + O_2 \rightarrow CH_3 + HOO . \qquad (B)$$

According to our knowledge, none of these reactions has been the topic of quantum chemical study. After selection of a convenient quantum chemical approach, the aim of this study is to determine the characteristics of potential surfaces of both competing reactions on the basis of transition state theory and to represent the temperature dependence of rate constants of both reactions.

## METHODICAL TESTS

Since emphasis is laid on reaction ($A$) in this study, the enthalpies of reactions involving carbenes have been used for preliminary valuation of the INDO, MINDO/3, and *ab initio* methods using the basis sets STO-3G and 4-31G. As the non-substituted carbenes and O$_2$ are in the ground triplet state and doublet radicals appear in reaction ($B$), it has been necessary to work in the UHF approach. The results of the metodical test are summarized in Table I. Either standard[5] or optimized geometries[6] were used for the INDO approximation. A part of the MINDO/3 as well as *ab initio* results[10-13] was also obtained from literature.

Though the reaction enthalpies in the INDO approximation decrease in the series given in Table I, their absolute values are highly overestimated in most cases. On the other hand, the MINDO/3 approach gives the best absolute values, but their order is not correct. The use of the *ab initio* approach in 4-31G basis appears to be the best compromise for the purpose of relative comparison of the rates of two reactions. In this case, a very good correlation (coefficient of correlation is 0·9976) has been obtained and the values of reaction heats exhibit correct order and are nearer to experimental values when compared with the results obtained by INDO and STO-3G. In accordance with the proposition put forward in paper[10], we have chosen the strategy of calculation which consists in calculating the least energy paths in the STO-3G basis, the geometry of the important points of hypersurface (minima and saddle points), and determining the energy of these points in the 4-31G base. The algorithms in the programme[15] GAUSSIAN-80 were used for finding the stationary points. The frequencies of individual vibration modes necessary for the zero-point-energy (ZPE) correction and calculation of the preexponential factor of rate constants were obtained in the MINDO/3 approximation by means of the programme[16] GEOMO-RV. The ZPE correction was not made for the energetic differences obtained by

TABLE I

Enthalpies of the reactions of carbenes in different quantum chemical approaches (kJ/mol)

| Reaction | exp.[a] | INDO | MINDO/3 | STO-3G | 4-31G |
|---|---|---|---|---|---|
| CH$_4$ → $\overline{\text{C}}$H$_2$ + H$_2$ | 351·0 | 2 137·2 | 445·6 | 622·6 | 532·1 |
| CH$_3$—CH$_3$ → CH$_3$—$\overline{\text{C}}$H + H$_2$ | 329·3 | 1 970·2 | 402·4 | 574·6 | 489·7 |
| CH$_3$—CH$_2$—CH$_3$ → CH$_3$—$\overline{\text{C}}$—CH$_3$ + H$_2$ | 307·5 | 1 854·3 | 385·1 | 540·5 | 455·5 |
| CH$_3$—CH$_2$—CH$_3$ → $\overline{\text{C}}$H$_2$ + CH$_3$—CH$_3$ | 297·1 | 1 517·1 | 440·3 | 546·1 | 439·4 |
| CH$_3$—CH$_3$ → $\overline{\text{C}}$H$_2$ + CH$_4$ | 286·2 | 1 525·9 | 475·8 | 543·7 | 435·5 |
| CH$_2$=CH$_2$ → CH$_3$—$\overline{\text{C}}$H | 192·0 | 515·1 | 239·2 | 273·3 | 313·9 |
| CH$_2$ = CH—CH$_3$ → CH$_3$—$\overline{\text{C}}$—CH$_3$ | 181·2 | 447·3 | 220·0 | 255·3 | 292·2 |
| CH$_2$(triplet) → CH$_2$(singlet) | 81·6[b] | 60·7 | 46·3 | 167·9 | 155·7 |

[a] Besides the last reaction, the data were taken from paper[3]. [b] Taken from paper[4].

MINDO/3 because the MINDO/3 parameters were fitted for experimental data without taking ZPE into account[14].

### Weak Interactions

In the first stage, we had to investigate a possible formation of weak complexes of the van der Waals type consisting of a methane molecule and oxygen molecule. We concentrated our attention on the type of geometries corresponding to entrance channels of reactions $(A)$ and $(B)$.

Two local minima in the STO-3G basis have been found for geometry represented in Fig. 1 by the use of optimization of 6 degrees of freedom in which $CH_4$ and $O_2$ are regarded as rigid molecules. Minimum $a)$ is situated on the pressumed pathway of reaction $(A)$. The bottom of the local minimum in the STO-3G basis is 0·5 kJ/mol over the energy of separated reactants whereas in the $4-31G$ base, it is 0·1 kJ/mol under this value. The join line of the $O_2$ nuclei is slightly deflected from the plane of symmetrical pentagon, *i.e.* by 1·5° about the centre of the O—O bond while the O···H distance is $3·5 . 10^{-10}$ m. Minimum $b)$ is situated in the entrance channel of reaction $(B)$. In the case, its bottom in the STO-3G basis is also situated 0·5 kJ/mol over the energy of isolated reactants whereas it is 14·6 kJ/mol under this value provided the $4-31G$ basis is used. The H···O distance on the linear connecting line C—H···O—O is $2·9 . 10^{-10}$ m. As these calculations have been performed with small bases where the probability of the error is high, it will be necessary to verify the shape of hypersurface in the region of above geometries by using greater bases and eventual inclusion of correlation effects. Though the existence of both minima need not significantly affect the rate of reactions $(A)$ and $(B)$, the confirmation of this existence may be of great importance in the field of photochemistry as well as in various biophysical and biochemical processes.
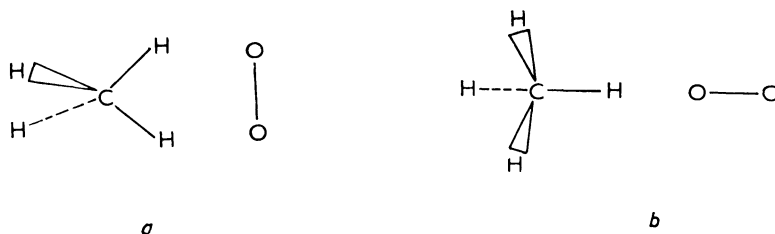


FIG. 1

Geometry of the Van der Waals complexes $(a)$ of the $CH_4$ and $O_2$ molecules $(b)$

*Characteristics of the Potential Energy Surfaces of Reactions* (A) *and* (B)

Reaction (A) giving rise to carbene as well as radical reaction (B) belongs among endothermic reactions. It means that already reaction enthalpies give information about the lower limit of activation barriers of both reactions. The values of $\Delta H$ for reactions (A) and (B) corresponding to the absolute zero temperature are listed in Table II. The experimental data were determined from the heats of formation by using JANAF tables[20]. A comparison shows that the enthalpy of reaction (A) is by 83·2 kJ/mol greater than that one of reaction (B). The best absolute values of $\Delta H$ are supplied by the MINDO/3 method.

The characterization of the potential energy surface in the region of saddle points is a much complicated problem. As the algorithm of searching for the saddle point in GAUSSIAN-80 is based on the Newton–Raphson-type method which functions well only at the start from geometries near to the saddle point, it was necessary in the first stage to localize the region of saddle point by the optimization of coordinates involving fixation of one coordinate used as reaction coordinate. In either case, the $r_{O...H}$ distance was chosen to be the reaction coordinate while it was assumed for reaction (A) that both $r_{O...H}$ distances are equal. As some weak minima were found in the region of entrance channel, the possibility of reaction pathway in the direction of the $r_{C-H}$ reaction coordinate was also examined. These reaction pathways, however, exhibited considerably greater activation barriers than those with the $r_{O...H}$ coordinate and, for this reason, they were not taken into consideration.

The geometry corresponding to the saddle point of reaction (A) is represented in Fig. 2. The height of activation barrier resulting from single-point calculation in the 4−31G basis is equal to 543 kJ/mol. For calculation of the rate constant, we used the value of 546 kJ/mol which results from the preceding value after correction for ZPE. The MINDO/3 method gives the value of 443 kJ/mol for that barrier.

The procedure for studying reaction (B) was analogous. The obtained geometry of the activated complex is represented in Fig. 3, the barrier of reaction is 273 kJ/mol

TABLE II

Enthalpies of reactions (A) and (B) at the temperature of absolute zero (kJ/mol)

| Reaction | STO-3G | 4-31G | MINDO/3 | Exp.[a] |
|----------|--------|-------|---------|---------|
| (A) | 400·2 | 270·6 | 292·9 | 323·0 |
| (B) | 217·8 | 166·9 | 201·7 | 239·0 |

[a] Ref. [20].

and after correction for ZPE 279 kJ/mol. The MINDO/3 barrier is equal to 216 kJ/mol.

A comparison of the data corresponding to both reactions indicates some interesting facts. First of all, the activated complex in reaction $(A)$ appears on the reaction pathway considerably earlier than in reaction $(B)$ $(r_{O\cdots H} = 1\cdot212 \cdot 10^{-10}$ m and $r_{C\cdots H} = 1\cdot45 \cdot 10^{-10}$ m for reaction $(A)$ and $1\cdot07$ and $1\cdot54$ for reaction $(B))$. Reaction $(B)$ is a typical representative of product-like-activated-complex reactions because the geometry of the $O$—$O\cdots H$ segment (Fig. 3) does not practically differ from the resulting geometry of the OOH radical. The activation barrier of reaction $(B)$ is somewhat higher than a half of the activation barrier of reaction $(A)$ which suggests the fact that the processes in the $C\cdots H\cdots O$ branches of reaction $(A)$ are independent of each other and the collective effects accompanying the formation of the activated complex, $e.g.$ ring strain, do not significantly affect the rate of reaction.

*Rate Constants*

The rate constants of reactions $(A)$ and $(B)$ were determined on the basis of the transition state theory by means of the known formula

$$ k = l \frac{k_B T}{h} \frac{Q^{\ddagger}}{Q_A Q_B} \exp\left(-\Delta H_0^{\ddagger}/RT\right), $$

where $Q_A$ and $Q_B$ are the partition functions of reactants, $Q^{\ddagger}$ is the partition function of the activated complex, and $\Delta H_0^{\ddagger}$ is the enthalpy of activation at the temperature of absolute zero. The influence of the tunneling effect on the rate of reactions $(A)$ and $(B)$ may be neglected at high temperatures. In both cases, an interesting role is played by the statistical factor $l$ which characterizes the number of the equivalent
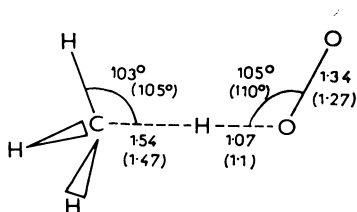


FIG. 2

Geometry of the saddle point for reaction $(A)$ for the STO-3G basis (the MINDO/3 values are given in parentheses)
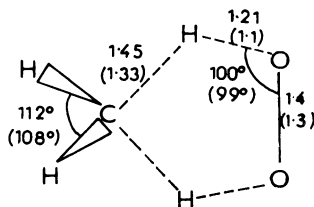


FIG. 3

Geometry of the saddle point for reaction $(B)$ for the STO-3G basis (the MINDO/3 values are given in parentheses)

activated complexes in the transition from reactants to products[21]. For reaction $(A)$, it assumes the value of 12 owing to six equivalent orientations of $CH_4$ and two equivalent orientations of $O_2$ in the activated complex as represented in Fig. 2. On the other hand, the activated complex of reaction $(B)$ (Fig. 3) has more possibilities. There are four orientations of $O_2$ and three equivalent planes of $O_2$ for rotation about the $C \cdots H \cdots O$ axis which gives the result $l = 24$. Assuming the character of the activated complexes does not considerably change in the progression to higher alkanes, the factor $l$ for reactions $(A)$ and $(B)$ shall assume the values of 6 and 18 for the $—CH_3$ group or 2 and 12 for the $—CH_2—$ group, respectively. That means in the case of long hydrocarbon chains that reaction $(B)$ is almost six-times more

TABLE III

Summarization of the results of calculation of the rate constants for reactions $(A)$ and $(B)$

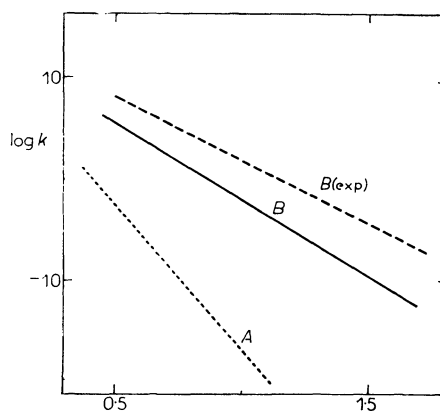| | Reaction $(A)$ | Reaction $(B)$ (exp. values[a] are in parentheses) | |
|---|---|---|---|
| ZPE correction (kJ/mol) | 3 | 7 | |
| $\Delta H_0^{\ddagger}$ (kJ/mol) | 546 | 279 | |
| $E_a$ (kJ/mol) | 549 | 284 | (234.3) |
| log $A$ | 11.9 | 12.8 | (13.9) |
| $k$ (cm³/mol s) | $8 . 10^{11} \exp. (-549/RT)$ | $6 . 10^{12} \exp (-284/RT)$ | |
| | | $(8 . 10^{13} \exp (-234\cdot3/RT))$ | |

[a] Ref.[18].



FIG. 4

Temperature dependence of the rate constants of reactions $(A)$ and $(B)$

probable from the stand-point of statistical distribution of orientation of reactants than reaction $(A)$.

The vibrational frequencies of reactants and activated complexes necessary for calculating the partition functions and ZPE corrections in the rigid-rotor-harmonic--oscillator approximation were obtained from the analysis of the MINDO/3 potential surface. The results of calculations of the rate constants are summarized in Table III and Fig. 4. The Arrhenius activation energy $E_a$ given in Table III was determined for the temperature region $400 - 2\ 100$ K. A comparison with the experimental data valid for reaction $(B)$ shows that the activation energy is overestimated by 50 kJ/mol while the value of preexponential factor is underestimated. Basevitch and coworkers[17] give a similar experimental value $E_a = 230 \cdot 1$ kJ/mpl. A comparison of the results found for reactions $(A)$ and $(B)$ leads to the conclusion that the reaction giving rise to the HOO radical in the thermal oxidation of hydrocarbons must have significant priority over the competing reaction producing $H_2O_2$ and carbene (at tem-temperatures of about $1\ 000$ K, the difference approximately corresponds to 12 decimal orders in the values of the rate constants found for the $CH_4$ molecule). This difference is caused by a great value of the activation energy and small value of the preexponential factor of reaction $(A)$. On the basis of this analysis, it is evident that we must seek other reactions throwing light on the origination of carbenes in hydrocarbon combustion. One of the alternatives may be the reaction of the double bond with $O_2$
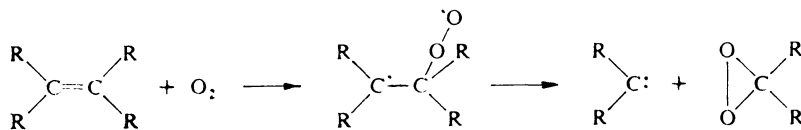


This possibility will be investigated by the methods of quantum chemistry in our subsequent studies.

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