

QUASICLASSICAL TRAJECTORY STUDY OF THE CH₂ + O₂ REACTION

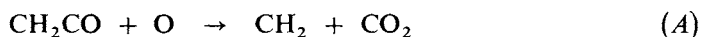
Ján URBAN, Viliam KLIMO and Jozef TIŇO

*Polymer Institute, Centre of Chemical Research,
Slovak Academy of Sciences, 842 36 Bratislava*

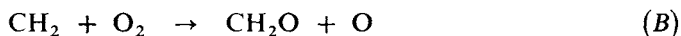
Received February 21st, 1986

The reaction of atomic oxygen formation from methylene and O₂ reactants was studied on the LEPS surface with Sato parameters determined by fitting *ab initio* points of the triplet reaction hypersurface. Besides the rate constant obtained from the analysis of classical trajectories, dynamic characteristics of the reaction have been determined.

The chemistry of carbenes is closely related to the reactions of their simplest member – methylene. This highly reactive radical has been identified in the flame of burning hydrocarbons¹, where it is of importance in branching and radical reactions. One of these is the interaction with molecular oxygen forming various products. Böhland *et al.*¹ studied the CH₂ + O₂ reaction experimentally and determined the total rate constant of this reaction. They did not directly measure reaction products of separate channels. They obtained CH₂ from ketene (reaction A) which was prepared with two sets of experimental conditions.



The concentration of ketene was low in one case and high in the other. In both cases equal reaction rates were observed, even though it is assumed that atomic oxygen was produced by the subsequent CH₂ + O₂ reaction. In the latter case enhancement of carbene formation and consequently a reaction rate change were expected. For this reason (and from other indirect observations) they concluded that the reaction channel (B) represents less than 10%.



On the other hand, Hatakeyama *et al.*² found CH₂O in the output channel from which they deduced that this reaction is likely. The aim of this paper is to investigate theoretically the course of the reaction wherein atomic oxygen is created. From the classical trajectory analysis on the energy hypersurface the rate constant and dynamic characteristics of the reaction are determined. Results obtained in this way may be

useful in forming a qualitative idea of the reaction dynamics of molecular oxygen, not only with CH_2 , but also with other carbenes in the triplet state in burning processes.

THEORETICAL

The interaction of methylene with molecular oxygen gives, in the first reaction step, methylene peroxide which belongs to the group of Criegee intermediates³. The triplet form of methylene peroxide, which is important for atomic oxygen and formaldehyde creation, is more stable in the planar configuration. Calculation of the heat of reaction based on the heat of formation of CH_2OO (ref.³) and CH_2 (ref.⁴) gives $-283.3 \text{ kJ mol}^{-1}$ for the intermediate formation, *i.e.* for the reaction



and $-251.2 \text{ kJ mol}^{-1}$ for the heat of reaction (B) as a whole. The zero point energy correction changes these values to $-311.3 \text{ kJ mol}^{-1}$ and $-265.4 \text{ kJ mol}^{-1}$ respectively. The depth of the energy minimum and the enthalpy of reaction (B) were the criteria for the reaction (B) triplet hypersurface determination. According to this, 36 points were calculated by the UMP2 method using a basis set⁵ with bond functions localized on the O—O and C—O bonds. Fitting of the LEPS surface was done by the gradient method. By using the least squares method, optimum values of the Sato parameters were determined. The methylene molecule was substituted by a quasiatom in this case. This is in agreement with the assumption that the geometric parameters of the CH_2 group of formaldehyde do not significantly differ in the course of reaction from those of methylene. Fitted values of the Sato parameters, Δ , and of the Morse parameters are given in Table I.

This LEPS surface gives a minimum reaction path barrier of 1 kJ mol^{-1} in the input channel, a minimum of $-314.6 \text{ kJ mol}^{-1}$ with respect to reactants, a barrier of 10 kJ mol^{-1} in the output channel, and the reaction enthalpy of -265 kJ mol^{-1} .

TABLE I
Morse and Sato parameters of the LEPS surface

Bond ^a	D_e , eV	β , 10^{10} m^{-1}	r_e , 10^{-10} m	Δ
O—O	5.21	2.65	1.207	0.79
R—O	7.97	2.3	1.21	0.16

^a R denotes a quasiatom.

The dioxymethylene complex has the following geometrical parameters $r_{\text{R-O}} = 1.22 \cdot 10^{-10}$ m and $r_{\text{O-O}} = 1.35 \cdot 10^{-10}$ m with the angle $\widehat{\text{COO}} = 100^\circ$. Karlström and Roos⁶ determined in MCSCF *ab initio* calculations $r_{\text{CO}} = 1.275 \cdot 10^{-10}$ m and $r_{\text{OO}} = 1.313 \cdot 10^{-10}$ m; their results differ only in the COO valence angle which has a value of 119.5° in their calculations.

The foregoing LEPS surface has been used for quasiclassical trajectory calculations, the details of which have previously been described in several papers⁷⁻⁸. Individual series of quasiclassical trajectories were calculated at energies from 0.02 eV up to 6 eV. In each of these series of trajectories the maximum value of the b_{max} impact parameter was determined. The largest value among them is $b_{\text{max}} = 2.9 \cdot 10^{-10}$ m. The initial vibration-rotation state of the oxygen molecule was that with vibrational quantum number $v = 0$ and rotational quantum number $J = 14$. This state represents the average value of the vibrational-rotational states of O_2 at burning temperatures⁹. In this vibrational-rotational state the oxygen molecule has $l_{\text{max}} = 1.273 \cdot 10^{-10}$ m and $l_{\text{min}} = 1.151 \cdot 10^{-10}$ m. Using the Monte Carlo method, other variables necessary for the calculation of the reaction probability for collisions were generated by random. Twelve Hamiltonian equations were integrated with the integration step $1.5 \cdot 10^{-16}$ s. The precision of the integration was controlled by conservation of the total energy and angular momentum. The vibration and rotation energies of the quasidiatomic molecules formed were determined by the analysis of the final states using the Muckerman method¹⁰. The lifetime of the complex is one of its important characteristics. It can be evaluated from the following relation¹¹

$$-\ln\left(\frac{N_\tau}{N_0}\right) = -\ln(\Delta\tau \cdot k_N) + k_N\tau, \quad (1)$$

where N_τ is the number of reactive trajectories in the time interval $\tau + \Delta\tau$ and N_0 is the number of reactive trajectories in the interval with the shortest time considered, $\tau_{\text{min}} + \Delta\tau$. The symbol k_N corresponds to the rate constant of the complex unimolecular decomposition. From the set of τ and N_τ values k_N^{-1} of CH_2OO decomposition at a chosen energy was determined. This corresponds to the mean life-time of the complex.

RESULTS AND DISCUSSIONS

The cross section values for the reaction producing the CH_2O molecule were obtained from the analysis of 300 trajectories at every relative translational energy. At selected energy values the number of trajectories was increased three times. The resulting difference in the calculated cross section values, however, was insignificant. Fig. 1 shows the dependence of the cross section on the relative translational energy E_T . Its maximum value is observed at $E_T = 0.03$ eV. This corresponds to an energy just

above the reaction barrier. At higher energies a strong decrease of the cross section appears. As dissociation trajectories of the $\text{CH}_2 + \text{O}_2 \rightarrow \text{CH}_2 + \text{O} + \text{O}$ type have their threshold energy ($D_e(\text{O}_2) = 5.21 \text{ eV}$) at the end of the translational energy range under investigation, this decrease is due to the relative increase of nonreactive trajectories.

At the energy $E_T = 0.03 \text{ eV}$, *i.e.* the maximum cross section energy, the life-time of the complex was studied using three times as many trajectories than in the other cases. From the graphical dependence of equation (1) shown in Fig. 2 the value of $k_N^{-1} = 1.9 \cdot 10^{-13} \text{ s}$ was determined. The angular distribution of products at energy $E_T = 0.03 \text{ eV}$ is given in Fig. 3, wherein it can be seen that the major part of the

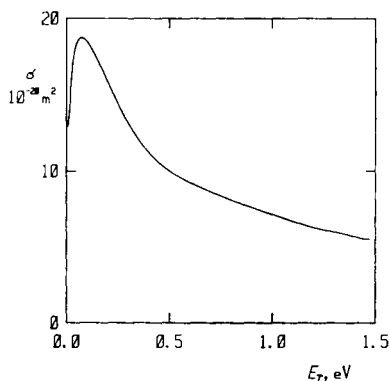


FIG. 1

Dependence of the total cross section σ on the relative translational energy E_T

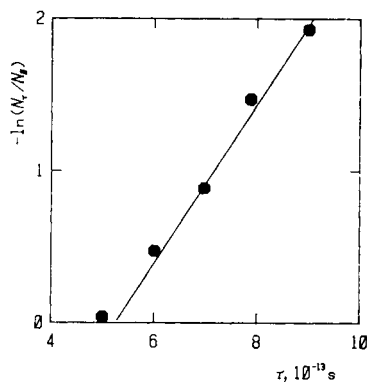


FIG. 2

Distribution of the life-time at relative translational energy $E_T = 0.03 \text{ eV}$

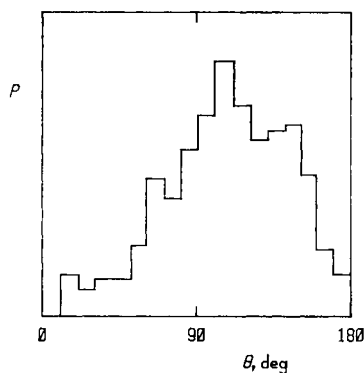


FIG. 3

Angular distribution of products at relative translational energy $E_T = 0.03 \text{ eV}$ (P denotes the probability of distribution to individual directions)

products exits at angles over 90°. This confirms the rebound mechanism typical for collisions at lower energies¹².

A high vibrational-rotational excitation is characteristic for the reaction products. At this energy we have $v' = 9$ and $J' = 26$. A similar situation occurs for the vibrational states of the RO molecule at other E_T values. Increasing the relative translational energy up to $E_T = 1.5$ eV the portion of vibrational energy varies from 0.7 to 0.6 of the total energy. Increasing E_T to 6 eV, the portion of vibrational energy decreases to 0.2. The portion of rotational energy, on the other hand, is 0.1 at low E_T energies and it reaches 0.4 of the total energy as E_T increases beyond 1.5 eV. The highly excited R—O bond (beyond the range of the model CH₂OO being a quasitriatomic molecule) is likely to lose a part of its energy by redistribution to other vibrational modes.

For a Maxwellian velocity distribution at temperature T and for a given (v, J) state of the oxygen molecule the temperature dependent rate constant k is given by

$$k(T, v, J) = g N_A (\pi \mu)^{-1/2} (2/kT)^{3/2} \int_0^\infty \sigma(E, v, J) e^{-E/kT} E dE, \quad (2)$$

where g is a degeneracy factor. From symmetry considerations for reaction (B) it follows that there are altogether 27 surfaces available, however only three of these lead to the products in question. Hence, the degeneracy factor value is 1/9. Based on the cross section values at individual energies E_T the following rate constant values at temperatures 300 K and 2 000 K have been evaluated

$$\begin{aligned} k(300 \text{ K}) &= 5.92 \cdot 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \\ k(2000 \text{ K}) &= 1.18 \cdot 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}. \end{aligned} \quad (3)$$

These temperature values were chosen expressly in order to compare the present results with the available experimental data. Böhland *et al.*¹ give a value $2.0 \pm 0.5 \cdot 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for the reaction CH₂ + O₂ rate constant at 296 K; Vinckier and Debruy¹³ give a value $9.03 \cdot 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 2 000 K. These values, which were determined by measuring the decrease of reactants and thus represent an average over all reaction channels, are not directly comparable with our results which correspond to reaction (B) only. Our values at both temperatures, however, are higher than the mean experimental rate constants. From this, and from the results reported in ref.², we conclude that reaction channel (B) can be important in the reaction of methylene with molecular oxygen. Secondary products of the CH₂ + O₂ reaction observed in ref.¹ can arise from consecutive reactions of O₂ and CH₂O (ref.³).

REFERENCES

1. Böhland T., Temps F., Wagner H. G.: *Ber. Bunsenges. Phys. Chem.* **88**, 455 (1984).
2. Hatakeyama S., Bandow H., Okuda M., Akimoto H.: *J. Phys. Chem.* **85**, 2249 (1981).
3. Herron J. T., Martinez R. I., Huie R. E.: *Int. J. Chem. Kinet.* **14**, 201, 225 (1982).
4. Stull D. R., Prophet H.: *JANAF Thermochemical Tables*, NSROS-NBS 37 (1971).
5. Klimo V., Tiño J.: *Mol. Phys.* **41**, 477 (1980).
6. Karlström G., Roos B.: *Chem. Phys. Lett.* **79**, 416 (1981).
7. Porter R. N., Raff L. M. in the book: *Modern Theoretical Chemistry* (W. H. Miller, Ed.), part B, p. 1. Plenum Press, New York 1976.
8. Truhlar D. G., Muckerman J. T. in the book: *Atom-Molecule Collision Theory: A Guide for the Experimentalist* (R. B. Bernstein, Ed.), p. 505. Plenum Press, New York 1979.
9. Kinnersley S. R., Murrell J. N.: *Mol. Phys.* **33**, 1479 (1977).
10. Muckerman J. T.: *J. Chem. Phys.* **54**, 1155 (1971).
11. Sorbie K. S., Murrell J. N.: *Mol. Phys.* **31**, 905 (1976).
12. Nikitin E. E., Zülicke L.: *Lecture Notes in Chemistry 8*. Springer, Berlin 1978.
13. Vinckier C., Debruyne W.: *J. Phys. Chem.* **83**, 2057 (1979).

Translated by P. Praena.