An MO-simulation of Elementary Reactions in Hydrocarbon Oxidation. I. A Bimolecular Coupling Reaction of the Methyl Radical and Molecular Oxygen

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An MO-simulation of the geometrical change in the bimolecular methane oxidation, $CH_3+O_2 \rightarrow CH_3O_2$, was performed using the CNDO/2 approximation. The geometry of CH_3O_2 was predicted to take $r_{OO}=1.19$ Å and $\angle COO=111°$ with fixed distances of $r_{CO}=1.44$ Å and $r_{CH}=1.09$ Å. The coupling reaction proceeds smoothly, without any appreciable activation energy, with the geometric transformation of the momentarily-living CH_3--O_2, with $r_{CO}=2.36\sim1.44$ Å, $r_{OO}=1.132\sim1.19$ Å, and $\angle COO=90\sim111°$. The magnitude of the electron migration between CH_3 and O_2 throughout the reaction was estimated.

Recent shock-tube[1,2] or ignition-delay[3,4] investigations have been concerned with methane oxidation involving the elementary bimolecular reaction of CH_3 and O_2, from the kinetic point of view.[5] Clark *et al.*[2] have reported the rate constant for the CH_3 and O_2 coupling reaction to be 1.987×10^7 M^{-1} s^{-1}, while Basco *et al.*[6] have evaluated the rate constant to be 2.7×10^8 M^{-1} s^{-1}; the coupling reaction may thus proceed very rapidly and easily. In this respect, the activation energy for the reaction has been estimated to be 18.0 kcal/mol by the ignition-delay investigation of Skinner *et al.*[4]

No theoretical investigation has, however, been concerned with the process of the coupling reaction of CH_3 and O_2 from the energetic and electronic points of view. Therefore, it is necessary to perform the MO-simulation for the $CH_3+O_2 \rightarrow CH_3O_2$ reaction.

The goal of the present investigation using the CNDO/2 theory[7] was to get a reliable prediction of the geometrical changes (and those of the electronic structures) of CH_3 and CH_3O_2 generated in the course of methane oxidation and to shed some light on the elementary bimolecular reaction of CH_3 and the $^3\Sigma_g^-$ state of O_2.

Method of Calculation

In this work, the following three systems were investigated: (a) the methyl radical, CH_3, (b) the methylperoxyl radical, CH_3O_2, and (c) the bimolecular coupling reaction of CH_3 and the $^3\Sigma_g^-$ O_2.

The geometric parameters are shown in the proper figures, but the interatomic distrances of C–H and C–O were fixed at 1.09 Å and 1.44 Å respectively for the sake of simplicity.

The method of calculation was CNDO/2, using the integrals and parametrization in Ref. 7.

Results and Discussion

Methyl Radical and Triplet Molecular Oxygen. The geometry of neutral CH_3 has long been known to take the "planar C_{3v}" (*viz.* D_{3h}) $^2A_2''$ state as the energetically most stable species. The vacuum UV spectroscopic study of Herzberg[8] gave the planar D_{3h} structure with the optimized bond length of C–H (r_{CH}), 1.079 Å, while some semiempirical[9] and nonempirical[10–12] treatments of CH_3 have favored a planar or nearly planar C_{3v} configuration.

The present CNDO/2 calculations on CH_3 at the angle of 70°32′∼90° between a C–H bond and a threefold axis suggest that the planar D_{3h} structure is most likely, as had been expected. Here, the predicted CH_3 geometry resulting from the semiempirical and *ab initio* calculations is summarized in Table 1 for the sake of comparison.

On the other hand, the equilibrium bond length of O–O in the $^3\Sigma_g^-$ O_2 has now been established to be 1.132 Å[7] (CNDO/2 calculation) or 1.207 Å[13] (experiment). The former value was used for the present MO-simulations.

The frontier orbitals of the singly-occupied (SO), nonbonding carbon 2p-orbital of the D_{3h} CH_3 (−13.188 eV) and of the doubly-degenerate SO $1\pi_g$-orbitals of O_2 (−14.856 eV) play a predominant role in the bimolecular coupling reaction of both species. The coupling reaction may be initially made possible by the maximum overlapping of the frontier orbitals mentioned above at the right angle of C–O–O (see below).

Methylperoxyl Radical. Neither the semiempirical nor the *ab initio* treatment has hitherto been concerned with the CH_3O_2 geometry, except in the case of an

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[1] T. P. J. Izod, G. B. Kistiakowsky, and S. Matsuda, *J. Chem. Phys.*, **55**, 4425 (1971).

[2] T. C. Clark, T. P. J. Izod, and S. Matsuda, *ibid.*, **55**, 4644 (1971).

[3] A. Lifshitz, K. Scheller, A. Burcat, and G. B. Skinner, *Combust. Flame*, **16**, 311 (1971).

[4] G. B. Skinner, A. Lifshitz, K. Scheller, and A. Burcat, *J. Chem. Phys.*, **56**, 3853 (1972).

[5] Other kinetic analyses of methane oxidation can be seen in the following references: R. M. R. Higgin and A. Williams, *Symp. Combust.*, 12th, Poitiers, France, **579** (1969); D. J. Seery and C. T. Bowman, *Combust. Flame*, **14**, 37 (1970); C. T. Bowman, *Combust. Sci. Technol.*, **2**, 161 (1970).

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[7] J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York (1970).

[8] G. Herzberg, *Proc. Roy. Soc., Ser. A*, **262**, 291 (1961).

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[10] K. Morokuma, L. Pederson, and M. Karplus, *ibid.*, **48**, 4801 (1968).

[11] W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **73**, 808 (1971).

[12] P. Millie and G. Berthier, *Int. J. Quantum Chem. Symp.*, No. 2, 67 (1968).

[13] G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, Princeton, N. J. (1950).

Table 1. Prediction of CH_3 geometry

Basis set	Configuration	r_{CH} (Å)	∠HCH (deg)	Reference
Present CNDO/2	planar $^2A_2''$	1.090	120	
INDO	nearly planar $^2A_1$	1.080	119.7	9
ab initio	planar $^2A_2''$	1.080	120	10
STO-3G	pyramidal $^2A_1$	1.080	118.3	11
4-31G	planar $^2A_2''$	1.070	120	11
Exptl.	planar $^2A_2''$	1.079	120	8

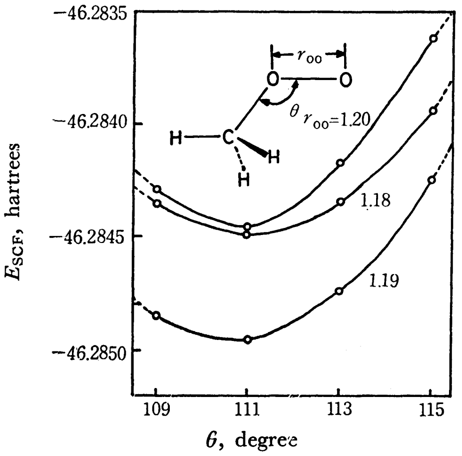


Fig. 1. SCF total energies E_{SCF} of CH_3O_2 as a function of two geometric parameters (r_{OO} and θ).

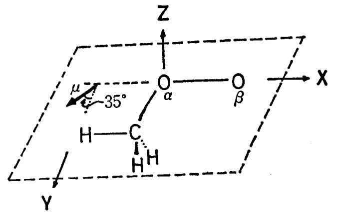
iterative extended Hückel MO treatment.[14] The CNDO/2 investigation is carried out on CH_3O_2 with the O–O bondlength (r_{OO}) of 1.15∼1.45 Å and the bond angle of C–O–O (θ) of 103∼115° under the fixed angle of HCH, 109°28′. Fig. 1 presents the SCF total energies, E_{SCF}, of CH_3O_2 as a function of two geometric parameters, r_{OO} and θ. As can be seen from Fig. 1, CH_3O_2 with $r_{OO}=1.19$ Å and $\theta=111°$ is shown to be the energetically most stable species. The predicted angle of 111° differs by only 3° from that of HO_2 (108°) obtained from the vibration spectrum study of Paukert and Johnston,[15] but it differs considerably from the HO_2 angle of 104.6°[16] predicted using the *ab initio* SCF–CI calculation.

On the other hand, our predicted O–O bond distance, 1.19 Å, is much closer to that of diatomic O_2 (1.207 Å[13]) than that of H_2O_2 (1.475 Å[17]) or HO_2 (1.458 Å[16]).

Table 2. Electronic property of CH_3O_2

Minimum energy, hartrees		−46.285
Bond length of O–O, Å		1.19
Bond length of C–O, Å		1.44
Bond angle of C–O–O, deg.		111
Dipole moment,[a] Debye		2.163
Ionization potential,[b] eV		13.83
g value		2.003
Electron density	O_α	6.032
	O_β	6.106
	C	3.899
AO electron density of O_β	p_x[c]	1.106
	p_y[c]	1.986
	p_z[c]	1.188

a) The direction of dipole moment (μ) is indicated below.
b) This is derived from the MO level of the highest occupied orbital of CH_3O_2.
c) As to the directions of orbital expansions, see the following figure:



Some remarks will be now made concerning the electronic property of CH_3O_2 on the basis of the computed results listed in Table 2. The estimated ionization potential of 13.83 eV is slightly less than that of 14.66 eV[18] found in HO_2. This may be in harmony with the opinion that the larger the alkyl group, R, in the RO_2 radical becomes, the more the ionization potential is lowered.[14] Moreover, the *g* value (2.003) computed by the Stone equation[21] is somewhat less than that of the experiment (2.015).[14]

Here, it may be worthy of emphasis that the expansion of the radical spin orbital is perpendicular to the cross-section of the C–O–O (xy-plane in Table 2).

Bimolecular Coupling Reaction of CH_3 *and* $^3\Sigma_g^-$ O_2. The interacting system of CH_3–O_2 has four geometric parameters,[22] *i.e.*, the bond lengths of O–O and C–O and the bond angles of C–O–O and H–C–O. The SCF total energies, E_{SCF}, as a function of the above four geometric parameters have only one minimum

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[14] O. Yamamoto, H. Kato, and T. Yonezawa, *Nippon Kagaku Zasshi*, **91**, 907 (1970).

[15] T. T. Paukert and H. S. Johnston, University of California Radiation Laboratory Report, No. UCRL-19109 (1969).

[16] D. H. Liskow, H. F. Schaefer III, and C. F. Bender, *J. Amer. Chem. Soc.*, **93**, 6734 (1971).

[17] R. H. Hunt, R. A. Leacock, C. W. Peters, and K. T. Hecht, *J. Chem. Phys.*, **42**, 1931 (1965).

[18] The ionization potential of the energetically most stable HO_2 ($r_{OO}=1.19$ Å, $r_{OH}=0.96$ Å, and the bond angle=111°) was estimated to be 14.66 eV by the CNDO/2 treatment (K. Ohkubo *et al.*, unpublished data). Experimentally, that of the HO_2 was found to be 11.53 eV[19] and/or 12.2 eV.[20]

[19] S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, **36**, 2681 (1962).

[20] A. J. B. Robertson, *Trans. Faraday Soc.*, **48**, 228 (1952).

[21] A. J. Stone, *Mol. Phys.*, **6**, 509 (1963).

[22] One unknown geometric parameter of the C–H interatomic distance can be settled uniformly to be 1.09 Å on the basis of usual C–H bond length (1.09 Å).[23]

[23] L. E. Sutton, Editor, "Interatomic Distances," The Chemical Society, London (1958).

Table 3. Electron densities of momentarily-living intermediate CH_3-O_2.[a]

Atom	AO	Electron densities as a function of C-O distance				
		∞	2.0 Å	1.8 Å	1.6 Å	1.44 Å
C	$p_y{}'$ [b]	1.000		0.838		0.858
	p_z	0.978	1.005	1.006	1.003	0.998
	net charge	4.097	3.984	3.961	3.932	3.899
H	s	0.968	0.966	0.971	0.978	0.989
O_α	s	1.802	1.780	1.746	1.698	1.644
	p_x	1.198	1.209	1.205	1.201	1.191
	p_y	1.500	1.273	1.292	1.339	1.402
	p_z	1.500	1.772	1.791	1.797	1.795
	net charge	6.000	6.034	6.034	6.035	6.032
O_β	s	1.802	1.818	1.821	1.822	1.822
	p_x	1.198	1.140	1.127	1.117	1.106
	p_y	1.500	1.910	1.949	1.976	1.986
	p_z	1.500	1.228	1.207	1.195	1.188
	net charge	6.000	6.096	6.104	6.110	6.106

a) The geometry of CH_3-O_2 is the same to that in Table 2.
b) The nonbonding carbon *p*-orbital of CH_3.

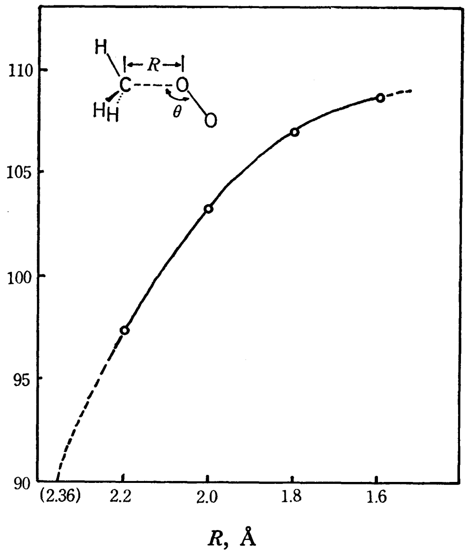

Fig. 2. Bond angle of C-O-O (θ) as a function of C-O distance (R) along the minimum potential barrier.

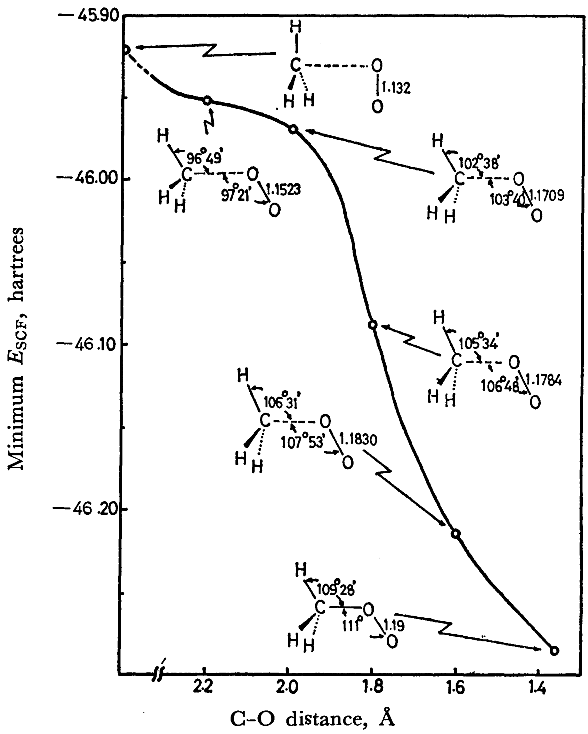

Fig. 3. Changes in minimum SCF total energies and configurations of CH_3--O_2 along the reaction path, $CH_3+O_2 \rightarrow CH_3$--$O_2$.

E_{SCF} value: this is an inevitable consequence from the basic quantum principle. The process of the coupling reaction of CH_3 and O_2 will, then, be estimated by gradually curtailing the C–O distance, giving attention to the minimum energy surface and the geometric transformation of the momentarily-living CH_3–O_2. The curve of the minimum E_{SCF} value as a function of the C–O distance is shown in Fig. 2, together with the configuration of CH_3–O_2. As Fig. 2 indicates, the coupling reaction proceeds smoothly, without any appreciable peak of the electronic energy path.

It is of interest to predict the C–O distance at the start of the reaction between CH_3 and O_2 before discussing the geometric transformation of CH_3–O_2. Bearing in mind the initial mode of the interaction between CH_3 and O_2 (*viz.*, ∠COO=90°), the abovementioned C–O distance surely corresponds to the *R* value (C–O distance) at ∠COO=90° under a minimum energy surface. Judging from the correlation between *R* and θ (angle of C–O–O) under such a minimum energy surface (see Fig. 2), the coupling reaction of CH_3 and O_2 should start at $R=2.36$ Å ($\theta=90°$).

With regard to the geometric transformation of CH_3—O_2 through the reaction progress, the following aspects are noticeable: slack expandings of ∠HCO and ∠COO with a gradual stretching of the O–O follows the hasty widening of both the angles with the lengthening of the O–O under $R<2.0$ Å (see Fig. 2).

Mention should also be made here of the electron migration between CH_3 and O_2 through the reaction. Taking into consideration the electron densities of the s and p orbitals on the carbon or oxygen atom (see Table 3), the predominant electron-migration can be depicted by the following representations.

The electron once transferred from the nonbonding half-occupied carbon p_y'-orbital to the O_α p_y-orbital through a $p\sigma$-type overlapping migrates further to the O_β p_y-orbital through $p\pi$-delocalization:

$$p_y'^{(C)} \xrightarrow{\text{through } p\sigma \text{ of C-O}\alpha} p_y^{(O\alpha)} \xrightarrow{\text{through } p_y\pi \text{ of } O_2} p_y^{(O\beta)}$$

There exists a back-donation from the O_β p_z-orbital to the O_α p_z-orbital through the $p\pi$-conjugation:

$$p_z^{(O\beta)} \xrightarrow{\text{through } p_z\pi \text{ of } O_2} p_z^{(O\alpha)}$$

However, further back-donation from the O_β p_z-orbital to the C p_z-orbital through the pseudo π orbital of the C–O_α bond cannot be expected, as may be seen from Table 3.

The calculations were carried out on a FACOM 230—60 computer at the Data Processing Center of Kyushu University.