A Semi-empirical MO Study of Radical-induced Decomposition of Dibenzoyl Peroxide. The Charge-transfer Character and Reaction Mechanism

Osamu KIKUCHI,* Keizo SUZUKI, and Katsumi TOKUMARU
Institute of Chemistry, The University of Tsukuba, Sakura-mura, Ibaraki 300-31
(Received September 30, 1977)

Radical-induced decomposition reactions of diacyl peroxides were investigated on the basis of the electronic structure of the peroxide-radical systems which were calculated using an approximate restricted open-shell SCF MO method in the MINDO/3 approximation, and on the basis of configuration analysis of the transition state of the reaction. For the transition state, (1) the change in peroxy O–O bond length is expected to be small, (2) the odd-electron density on the leaving group of the S_H2 displacement is expected to be very small, although appreciable odd-electron delocalization from the radical to the peroxide was observed, (3) the charge-transfer (CT) interactions which correspond to electron transfer from the radical to the peroxide was found to be important in the transition state. The trends observed in the orbital energies of the LUMO of substituted dibenzoyl peroxides and in the CT character of the transition state, which involves the singly-occupied MO of the radical and the $2p\sigma^*$ MO of the peroxide, agree well with the experimental facts, and strongly support a previous postulate that an important role is played by the $2p\sigma^*$ MO of the peroxy O–O group in the reaction.

Dibenzoyl peroxide (BPO) is one of the most frequently used sources of free radicals,[1] and its various modes of decomposition are an interesting subject of investigation. One typical process involving BPO is redical-induced decomposition:

$$\mathrm{Ph{-}\overset{O}{\overset{\|}{C}}{-}O{-}O{-}\overset{O}{\overset{\|}{C}}{-}Ph} + \cdot R' \longrightarrow \mathrm{Ph{-}\overset{O}{\overset{\|}{C}}{-}OR'} + \mathrm{Ph{-}\overset{O}{\overset{\|}{C}}{-}O}\cdot \qquad (1)$$

Extensive experimental studies[1-4] have contributed to the elucidation of the mechanism of this reaction. Step (1) is S_H2 substitution in which the radical attack occurs at the peroxy oxygen atom.[2] An electron-withdrawing substituent in BPO[3] and an electron-donating substituent in the radical[4] both enhance the reaction rate. The ionic character of the transition state of (1) has been pointed out.[3] The mechanism of step (1) has theoretically been considered by Tokumaru and Simamura[5] on the basis of experimental facts regarding the induced decomposition of peroxides by radicals. It has been suggested[5] that an interaction of the charge-transfer (CT) type, involving a singly-occupied MO (SOMO) of the attacking radical and the $2p\sigma^*$ antibonding orbital of the peroxy oxygen atoms, contributes to a lowering of the activation energy of the reaction.

In spite of these extensive experimental studies and qualitative explanations of the mechanism, no MO-theoretical investigations of the interacting BPO-radical system have been reported.[6] The purposes of the present note are: (i) to examine the reaction path of the radical-induced decomposition of BPO by means of a restricted open-shell method in the MINDO/3 approximation; (ii) to clarify the electronic structure of the transition state by means of configuration analysis for the wavefunction of the transition state, and (iii) to elucidate the substituent effect on the induced decomposition of BPO.

Method of Calculation

The electronic structure of the peroxide-radical systems were calculated in an approximate SCF version for open-shell systems which was proposed by Longuet-Higgins and Pople[7] and which has since been applied to all-valence-electron systems by one of the present authors.[8] For evaluating the electron integrals involved, the MINDO/3 approximation[9] was employed. The size of the BPO-radical system is too large to permit solving the problem even if the semi-empirical method is employed. In the present study, the reaction mechanism and the electronic structure of the transition state were considered using rather drastic approximations for the model system and its molecular structure. Diformyl peroxide (FPO), the simplest diacyl peroxide, and the methyl radical were adopted as model substances. The molecular parameters of the –COO group were fixed to those of BPO which were reported in a previous paper,[10] and a value of 90°[11] was used for the dihedral angle between the two RCOO planes. The conformation of C_{3v} CH_3 was optimized during the course of the reaction, the CH bond length being fixed at 1.087 Å, the optimized value for the D_{3h} methyl radical.

The substituent effect on radical-induced decomposition of BPO was elucidated on the basis of the electronic structure of substituted BPO in isolated states and on the basis of the CT character of the transition state of the BPO-methyl system. It is of note that CT from the radical to BPO will be underestimated in the transition state, since the ionization potential of the methyl radical is very large in comparison with those of the radicals currently used in actual experimental studies.

Configuration analysis was performed to clarify the electronic structure of the transition state. The wave function of the transition state (Ψ_T) was expanded in terms of doublet configurations (Ψ°) constructed from reference MO of the peroxide and of the planar methyl radical, thus

$$\Psi_T = C_g\Psi^\circ_g + \sum_i\sum_k C_{ik}\Psi^\circ_{i\to k} + \sum_j\sum_l C_{jl}\Psi^\circ_{j\to l} + \sum_j C_{jm}\Psi^\circ_{j\to m} + \sum_l C_{ml}\Psi^\circ_{m\to l} + \sum_k C_{mk}\Psi^\circ_{m\to k} + \sum_i C_{im}\Psi^\circ_{i\to m} + \sum_i\sum_l C_{il}\Psi^\circ_{i\to l} + \sum_j\sum_k C_{jk}\Psi^\circ_{j\to k}, \qquad (2)$$

where Ψ°_g is the slater determinant for the ground-state

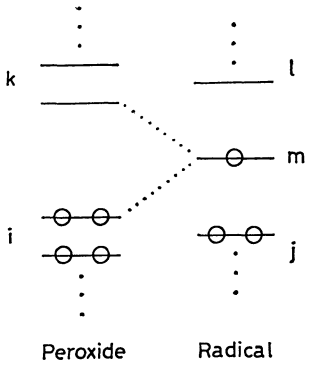


Fig. 1. Orbital interaction between a closed-shell molecule and a radical.

configuration of the peroxide-radical system, $\Psi^{\circ}_{i\to k}$ corresponds to one-electron exitation of the peroxide, $\Psi^{\circ}_{j\to l}$ $\Psi^{\circ}_{j\to m}$, and $\Psi^{\circ}_{m\to l}$ correspond to one-electron excitation of the radical, and the last four terms are CT configurations between the peroxide and the radical. The definition of indices, i, j, k, l, and m is given in Fig. 1. In Eq. 2, $\Psi^{\circ}_{a\to b}$ $(a\neq m,\ b\neq m)$ includes two independent wave functions corresponding to the $a\to b$ excited configuration. Neglecting the overlap between the MO in different molecules, the expansion coefficients in Eq. 2 were calculated using the following equations which were derived from the general formula given by Baba *et al.*,[12]

$$\begin{aligned} C_{a\to m} &= D^{m}_{0}D^{m-1}_{am}, \\ C_{m\to b} &= D^{m}_{mb}D^{m-1}_{0}, \quad (a\neq m,\ b\neq m) \\ C_{a\to b} &= (f_1^2+f_2^2)^{1/2}, \qquad (3) \\ f_1 &= \frac{1}{\sqrt{2}}\{D^{m}_{0}D^{m-1}_{ab}+D^{m}_{ab}D^{m-1}_{0}\} \end{aligned}$$

and $$f_2 = \frac{1}{\sqrt{6}}\{D^{m}_{0}D^{m-1}_{ab}-D^{m}_{ab}D^{m-1}_{0}+2D^{m}_{mb}D^{m-1}_{am}\},$$

where $D_0{}^m$ is the determinant derived from the occupied α-spin MO of the interacting and non-interacting peroxide-radical systems, and $D_0{}^{m-1}$ is that derived from the β-spin MO of the systems. The other notations are same as those given in Ref. 12.

Results and Discussion

Reaction Path. The decomposition of FPO induced by the methyl radical was examined. Since the radical attack occurs at one of the peroxy oxygen atoms,[2] several interacting patterns, shown in Fig. 2, were examined. The interaction energy for each pattern was calculated by changing the distance between the peroxy oxygen atom and the methyl carbon atom. The conformation of the methyl radical is fixed for each pattern so that the SOMO of CH_3 is directed toward the oxygen atom to be attacked. The interaction energies at $R_{O\text{-}C}=2.0$ Å are shown in Fig. 2. When the radical attack occurs within the HCOO plane (Fig. 2, A—C), attack from the C direction is the most favorable. However, the C pattern of interaction is not expected in actual systems such as the BPO-triphenylmethyl system, since the large substituents in the peroxide and in the radical make this approach impossible.

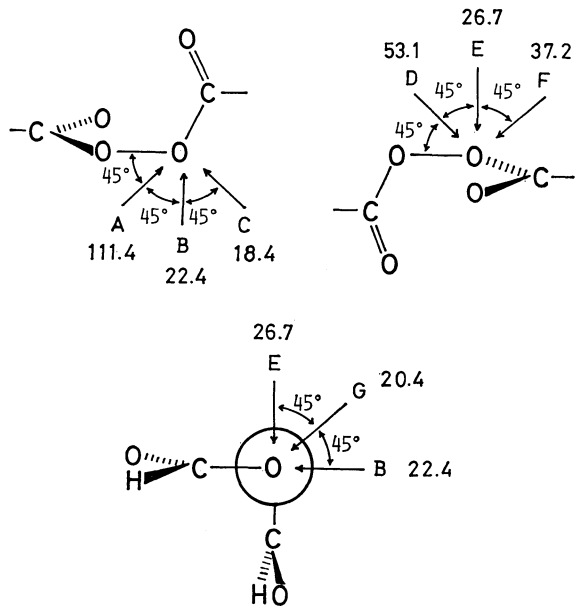


Fig. 2. Several interaction patterns between FPO and the methyl radical, and their interaction energies (kcal/mol) calculated at O–C=2.0 Å.

The G-pattern, for which the radical attack occurs in the plane which bisects the dihedral angle between the two RCOO planes and which is perpendicular to the peroxy O–O bond, may be most favorable in actual BPO-radical systems.

The potential energy surface for the G-approach[13] was calculated as a function of the peroxy O–O distance and of the O–C distance, other molecular parameters in FPO being fixed. The energy map obtained is shown in Fig. 3. For the transition state, the change (0.03 Å)

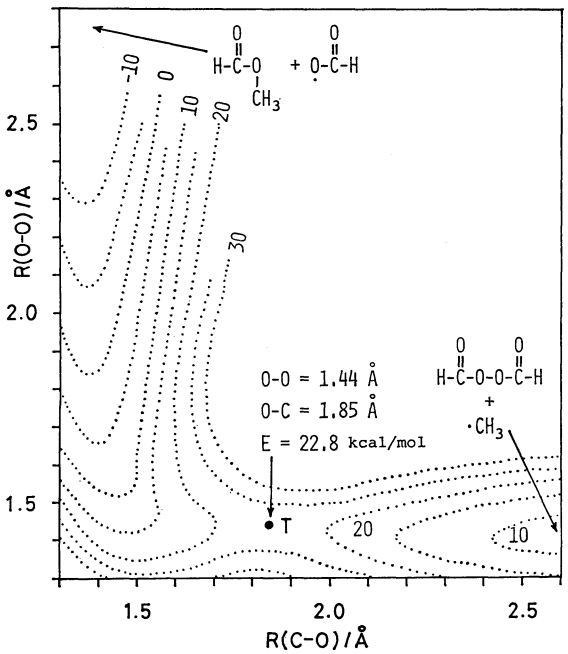


Fig. 3. Energy contours for the FPO–CH_3 system. The zero of energy (kcal/mol) is that of (FPO+CH_3) at infinite distance.

in the peroxy O–O bond length is expected to be small, while the O–C separation is large. The activation energy was estimated to be 23 kcal/mol which is somewhat larger than the observed values ($\simeq$10 kcal/mol, solvent dependent).[1,3]

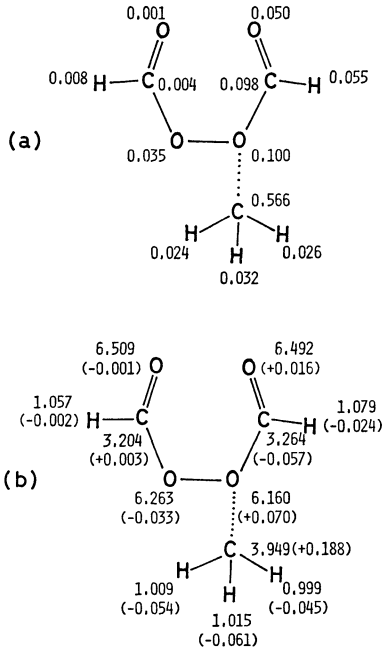
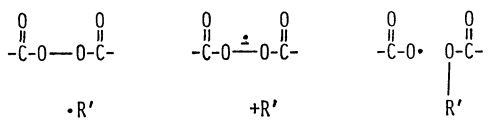


Fig. 4. Atomic spin densities (a) and atomic electron densities (b) of the FPO–CH_3 system in its transition state. The increases of the net charges are shown in parentheses.

Electronic Structure of the Transition State. The odd-electron and atomic electron distributions of the transition state are shown in Fig. 4. The changes in the atomic net charge densities caused by the peroxide-radical interaction are also shown in Fig. 4-b. Although large odd-electron delocalizations (35%) from the methyl radical to FPO are observed in the transition state, the odd-electron density on the leaving HCOO group is very small. This indicates that the contribution of structure III to the transition state is small. The ionic character of the transition state, for which the attacking group acts as an electron-donor, has been pointed out by Suehiro *et al.*[3] From Fig. 4, an ionic character is expected for the transition state, although its magnitude is not large for the present model system. The electronic structure of the transition state can thus be expressed as three structures, I, II, and III, whose contributions are in the order: I$\gg$II$>$III. This does *not* imply that the decomposition of diacyl peroxide by a radical gives the CT intermediate and then the carbonium ion (+R′)



I II III

as reaction products. The contribution of II to the electronic structure of the transition state would be larger in actual BPO-radical systems, such as the BPO-triphenylmethyl system, than in the present model system, because the methyl radical is a poorer electron donor than the substituted alkyl radicals.

Configuration Analysis. As may be seen from the general interaction scheme (Fig. 1) between a closed-shell molecule and a radical, the SOMO interactions of CH_3 with both the occupied and unoccupied MO of FPO are expected to be very important for the transition state of the reaction. This was demonstrated by the configuration analysis, in which the wave function of the transition state was expressed in terms of the reference wave functions constructed of the MO of two non-interacting molecules. The electron configurations of the C_2 FPO and D_{3h} CH_3 are:

for FPO (^{1}A), $\cdots(8b)^2(9a)^2(9b)^0(10a)^0\cdots$

and for CH_3 ($^2A_2''$), $\cdots(a_2'')^1(2a_1')^0\cdots$

The qualitative pictures of three MO of FPO are shown in Fig. 5. The a_2'' orbital is the SOMO of the methyl radical. All the "one-electron excited" and "one-electron transfered" configurations of the two reactants were employed in the expansion of the wave function of the transition state. The contributions calculated are listed in Table 1. Since the total contribution accounts for 97%, the contributions of other configurations are small.

The contribution of the ground-state configuration (Ψ_g°) is dominant (48%). The large contribution due to the polarization ($\Psi_{m\to t}^\circ$) of the CH_3 radical comes from the geometrical change of CH_3 from D_{3h} to C_{3v} for the transition state.[14] The CT configurations from FPO to CH_3 (15%) are very important for the transition state, while the polarization interactions for FPO ($\Psi_{i\to k}^\circ$) are relatively small. It is notable that the most important of the CT configurations corresponds to electron transfer from the SOMO of the radical to the LUMO of the peroxide, which has an anti-bonding character with respect to the peroxy O–O bond. This supports the assumption that CT plays an important

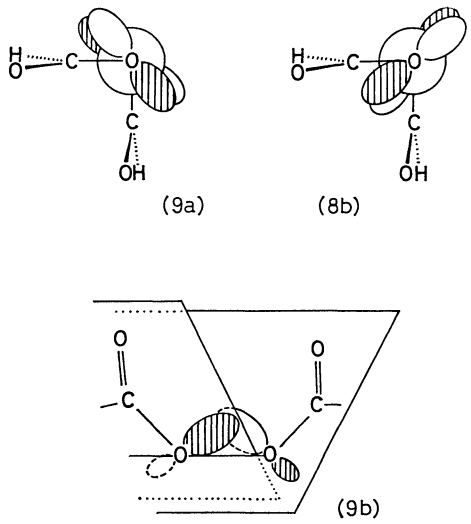


Fig. 5. Qualitative pictures of three MO's of FPO. The shape of each MO is drawn only in the peroxy oxygen region.

Table 1. Configuration analysis of the wave function of the FPO–CH_3 system for the transition state

Character of configurations[a]	Weight	Main configurations	Weight
ground	0.4798	ground	0.4798
$i \rightarrow m$	0.0824	$8b \rightarrow a_2''$	0.0319
		$4a \rightarrow a_2''$	0.0192
		$7a \rightarrow a_2''$	0.0157
$j \rightarrow m$	0.0087	—	—
$m \rightarrow k$	0.1489	$a_2'' \rightarrow 9b$	0.1005
		$a_2'' \rightarrow 10a$	0.0300
$m \rightarrow l$	0.1489	$a_2'' \rightarrow 2a_1'$	0.1487
$i \rightarrow k$	0.0467	$8b \rightarrow 9b$	0.0109
$j \rightarrow l$	0.0041	—	—
$i \rightarrow l$	0.0430	$8b \rightarrow 2a_1'$	0.0169
$j \rightarrow k$	0.0115	—	—
Total	0.9739		

a) i denotes the 17 occupied MO of FPO, j the 3 occupied MO of CH_3, k the 9 unoccupied MO of FPO, l the 3 unoccupied MO of CH_3, and m the singly-occupied MO of CH_3. Thus, $m \rightarrow k$, for example, indicates all the configurations which correspond to charge-transfer configurations from the SOMO of CH_3 to the unoccupied MO of FPO.

role in the induced decomposition of peroxides, as has been suggested by Tokumaru and Simamura.[5]

Substituent Effect on the Induced Decomposition of BPO. The rate constant of the induced decomposition of BPO is enhanced by an electron-withdrawing group in the phenyl group.[3] The important CT interaction at the transition state indicates that the electron-withdrawing group lowers the energy level of the $2p\sigma^*$ orbital of the peroxy O–O bond and increases the CT character of the transition state of the BPO-radical system. The orbital energies of several substituted BPO were calculated for predicted geometries.[10] The results are shown in Table 2. Strictly speaking, the LUMO of BPO is not the $2p\sigma^*$ of the peroxy O–O bond but is an unoccupied MO of the phenyl groups. In Table 2, the unoccupied MO which correspond to the $2p\sigma^*$ MO of FPO are called "LUMO." A very clear correlation between the orbital energies of the LUMO of substituted BPO and the electron-withdrawing character of the substituent is seen in Table 2. The CT character of the transition state was calculated using the geometry estimated for the FPO–CH_3 system. The CT interaction of the *p,p'*-dinitro BPO and CH_3 system is larger than that of unsubstituted BPO, while that for the *p,p'*-dimethoxy BPO–CH_4 system is smaller. This trend is parallel to that observed for the orbital energies of the LUMO of substituted BPO. The trends observed for the orbital energies of the LUMO of substituted BPO and for the CT character of the transition state agree well with the prediction given by Tokumaru and Simamura.[5]

Table 2. Orbital energies of the LUMO and the CT character of the transition state for *p,p'*-di-substituted BPO

Substituents *p*-	Substituents *p'*-	ε(LUMO)[a]	CT character for the transition state $m \rightarrow k$[b]	CT character for the transition state $m \rightarrow \sigma^*$[c]
OCH_3	OCH_3	1.154 eV	10.2%	7.0%
CH_3	CH_3	1.060	—	—
H	H	1.002	10.5	7.1
CN	CN	0.858	—	—
NO_2	NO_2	0.250	11.7	7.9

a) Orbital energies calculated for the equilibrium geometries predicted by MINDO/3.[10] The LUMO corresponds to the 9b orbital of FPO. b) All the configurations corresponding to the CT configurations from the SOMO of CH_3 to the unoccupied MO of BPO. c) All the configurations corresponding to the CT configurations from the SOMO of CH_3 to the unoccupied MO of BPO, which have the anti-bonding character of the peroxy O–O σ bond.

One of the authors, O. K., wishes to express his thanks to Dr. Ken Fujimori for useful discussions.

References

1) R. Hiatt, "Organic Peroxides II," ed by D. Swern,, Wiley-Interscience, New York (1971), p. 799; T. Koenig "Free Radicals I," ed by J. K. Kochi, John Wiley & Sons New York (1973), p. 133; Y. Ogata, "Chemistry of Organic Peroxides," Nankodo, Tokyo (1971), p. 170.

2) D. B. Denney and G. Feig, *J. Am. Chem. Soc.*, **81**, 5322 (1959); W. von E. Doering, K. Okamoto, and H. Krauch, *J. Am. Chem. Soc.*, **82**, 3579 (1960); W. P. Neuman and K. Rubsamen, *Chem. Ber.*, **100**, 1621 (1967).

3) K. F. O'Driscoll and P. J. White, *J. Polym. Sci., Part A*, **3**, 283 (1965); T. Suehiro, A. Kanoya, M. Omori, and T. Komori, *Bull. Chem. Soc. Jpn.*, **40**, 668 (1967).

4) S. Kato and F. Mashio, *Kogyo Kagaku Zasshi*, **59**, 380 (1956).

5) (a) K. Tokumaru and O. Simamura, *Bull. Chem. Soc., Jpn.*, **36**, 333 (1963); (b) K. Tokumaru, *Nippon Kagaku Zasshi*, **92**, 887 (1971).

6) The electronic structures of the peroxy O–O bonds in alkyl peroxides, peroxyacids, and peroxyesters have been investigated using the extended HMO method by T. Yonezawa, O. Yamamoto, H. Kato, and K. Fukui, *Nippon Kagaku Zasshi*, **87**, 26 (1966)) and by T. Yonezawa, H. Kato, and O. Yamamoto (*Bull. Chem. Soc. Jpn.*, **40**, 307 (1967)). The potential curves along the peroxy O-O bond cleavage of H_2O_2 have recently been obtained using CNDO/2-CI calculations by E.M. Evleth (*J. Am. Chem. Soc.*, **98**, 1637 (1976)).

7) H. C. Longuet-Higgins and J. A. Pople, *Proc. Phys. Soc.*, **68**, 591 (1955).

8) O. Kikuchi, *Bull. Chem. Soc. Jpn.*, **42**, 47 (1969).

9) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285, 1294, 1302, 1307 (1975).

10) O. Kikuchi, A. Hiyama, H. Yoshida, and K. Suzuki, *Bull. Chem. Soc. Jpn.*, **51**, 11 (1978).

11) X-Ray studies of dibenzoyl peroxide and acetylbenzoyl peroxide indicate a dihedral angle of about 90° (See G. A. Jeffery, R. K. McMullan, and M. Sax, *J. Am. Chem. Soc.*, **86**, 949 (1964), M. Sax and R. K. McMullan, *Acta Crystallogr.*, **22**, 281 (1964) and N. J. Karch, E. T. Koh, B. L. Whitsel, and J. M. McBride, *J. Am. Chem. Soc.*, **97**, 6729 (1975)), while MINDO/3 calculations give a value of 115° (Ref. 10).

12) H. Baba, S. Suzuki, and T. Takemura, *J. Chem. Phys.*, **50**, 2078 (1969).

13) The approach of the methyl radical from the in-plane B-direction gave a similar potential map.

14) The conformation of the FPO fragment for the transition state closely resembles the isolated FPO, while that of CH_3 (C_{3v} with an angle of 109° between the symmetry axis and each C-H bond) differs considerably from the planar CH_3 structure. The large contribution of the $m \rightarrow l$ configurations in Table 1 come from the direct application of configuration analysis[12] to the process accompanied by molecular deformation. When sp^3, instead of planar, conformation, was used as the reference structure of the methyl radical, the contribution of the $m \rightarrow l$ configurations was very small; in this case, all other features appeared in Table 1 and the conclusions obtained here remain unaffected. For a more correct treatment of the configuration analysis for the process accompanied by molecular deformation, see Ref. 15.

15) T. Okada, S. Nagase, K. Yamaguchi, and T. Fueno, *Bull. Chem. Soc. Jpn.*, **49**, 2377 (1976).