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MNDO MO THEORETICAL STUDY OF ELECTRONIC STRUCTURE AND HOMOLYTIC
DISSOCIATION OF PERFLUOROALKANOYL PEROXIDES

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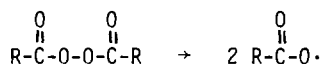
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SUMMARY

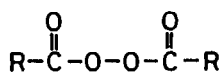
The MNDO molecular orbital method was applied to alkanoyl peroxides and the effect of fluorination on the electronic structure and the rate of the homolytic O-O cleavage of alkanoyl peroxides were analyzed. The fluorine atom introduced at the α carbon atom makes the peroxy O-O bond long and the dihedral angle between two COO planes large. The analysis of two-atom energy and its components energies has shown that the rate of the O-O cleavage correlates well with the destabilization of the resonance energy of the O-O bond and not with the electrostatic energy. The effect of elongation of the perfluoroalkyl group is also well elucidated by the two-atom energy. The perfluoroalkyl group lowers the $\sigma^*(O-O)$ anti-bonding orbital considerably, and this fully explains the observed rate of induced decomposition of perfluoroalkanoyl peroxides with benzene.

INTRODUCTION

Diacyl peroxides undergo a variety of reactions because of the weak peroxy O-O bond. A typical process is the homolytic cleavage of the O-O bond to form acyloxy radicals[1].



Zhao et al.[2] have shown that the introduction of fluorine atoms into the alkyl group in a diacyl peroxide changes considerably the rate of decomposition of the diacyl peroxide; the activation enthalpy of the decomposition of a perfluoroalkanyl peroxide is lower than that of the corresponding nonfluorinated alkanoyl peroxide by 5 ~ 8 kcal/mol. However, this interesting behaviour of perfluorinated alkanoyl peroxides has not been clarified. This study examines the electronic structure of perfluorinated alkanoyl peroxides based on the MNDO molecular orbital (MO) calculations and elucidates their reactivity of the homolytic O-O cleavage. Alkanoyl peroxides considered in this study are 1 ~ 10.



- | | |
|--|---|
| 1, R = CH ₃ | 6, R = CF ₂ CF ₃ |
| 2, R = CF ₃ | 7, R = (CH ₂) ₂ CH ₃ |
| 3, R = CH ₂ CH ₃ | 8, R = (CH ₂) ₆ CH ₃ |
| 4, R = CH ₂ CF ₃ | 9, R = (CF ₂) ₂ CF ₃ |
| 5, R = CF ₂ CH ₃ | 10, R = (CF ₂) ₆ CF ₃ |

They will make clear the effects of fluorination at the α and/or β carbon atoms and the effect of elongation of perfluoroalkyl groups.

METHOD

Alkanoyl peroxides considered here are large in size and semi-empirical methods are appropriate for MO calculations. The MNDO method has been pointed out to give too short peroxy O-O bond length and to overestimate the interaction between fluorine atoms[3]. We have shown that MINDO/3 method gives an appropriate peroxy O-O bond lengths and correct dihedral angle between two COO planes for diacyl peroxides[4]. Although MNDO gives a shorter O-O bond length for 1, both MNDO and MINDO/3 give similar stable conformation and similar conformational dependence of the electronic structure of 1. Thus the short O-O distance estimated by MNDO is not serious for our present purpose which intends to examine the substituent effect on the electronic structure of alkanoyl peroxides qualitatively. MNDO was adopted, since it is better than MINDO/3 for the compounds containing fluorine atoms[3].

The total energy of a molecule can be partitioned into one-atom and two-atom terms,

$$E_{\text{total}} = \sum_A E_A + \sum_{A>B} E_{A,B}$$

$$E_{A,B} = E_{A,B}^R + E_{A,B}^K + E_{A,B}^{ES}$$

where $E_{A,B}^R$, $E_{A,B}^K$ and $E_{A,B}^{ES}$ are resonance, exchange and electrostatic energies, respectively. The equations of these energy components have been given for the INDO approximation[5], and those for the MNDO approximation were derived similarly. These energy components reflect the bonding character between A and B atoms and can be used for the reactivity analysis.

MOLECULAR STRUCTURE AND ENERGY

Conformation of 1 and 2

The energy dependence of 1 on the rotation angles indicated in Fig. 1 was examined carefully, and then the molecular structure of 1 was optimized. The lowest-energy conformation is shown in Fig. 2 which is similar to the MINDO/3 conformation[4]. It has the planar O-C=O structure ($\theta_2=0$) and the *trans* conformation ($\theta_3=0$). The barrier to rotation of the methyl group was calculated to be 0.7 kcal/mol. As was pointed out above, the calculated O-O distance is shorter than the observed one by 0.17 Å.

The conformation of 2 was examined similarly. The lowest-energy conformation (Fig. 3) has $\theta_2=\theta_3=0$. The barrier to rotation of the CF_3 group is 1.6 kcal/mol. The C_2-C_4 distance in 2 was calculated to be longer than that in 1. This is the trend observed in fluorinated compounds calculated by MINDO[3]. The O-O distance and the dihedral angle, θ_1 , of 2 are larger than 1 and these are the effect of fluorine atoms.

Conformation of 3 ~ 10

For 3, 4, 5 and 6, the conformation with $\theta_3=\theta_4=0$ is stable; this *trans* conformation is denoted by "A conformation". The local minimum conformations were also found near $\theta_3=\theta_5=\pm 90^\circ$. Some of these have the energy which is lower than the A conformation. However, the energy difference among these minimum-energy conformations is very small, 0.5 ~ 1.0 kcal/mol, and it is convenient to use the same conformation for all alkanoyl peroxides to compare their electronic structure and reactivity. Thus the A conformations are compared in Table 1.

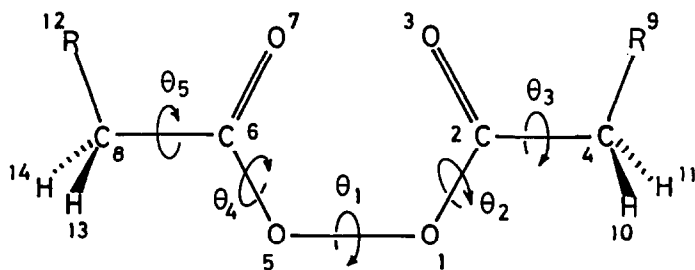


Fig.1. Numbering of atoms and definition of rotation angles for alkanoyl peroxides. The conformation shown corresponds to the conformation for $\theta_1=\theta_2=\theta_3=\theta_4=\theta_5=0$.

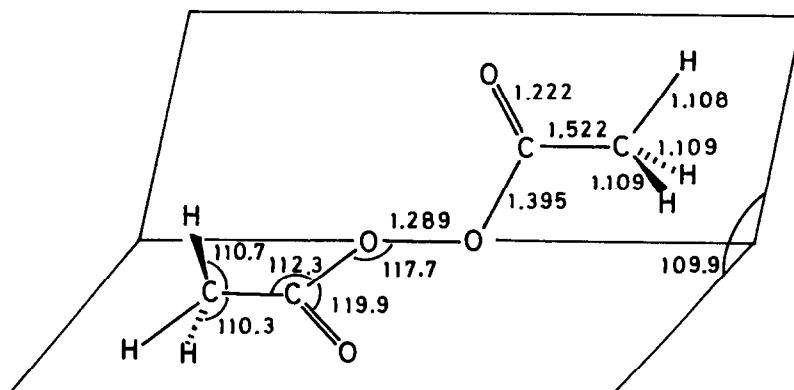


Fig.2. MND0 structure of diacetyl peroxide, 1. Bond lengths are in Å and angles are in degrees.

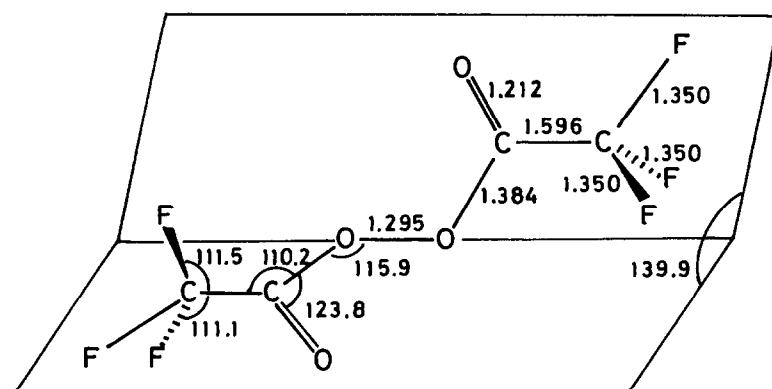


Fig.3. MND0 structure of hexafluorodiacetyl peroxide, 2. Bond lengths are in Å and angles are in degrees.

TABLE 1

MNDO molecular structures of alkanoyl peroxides.

Compound	Bond lengths				Angles			
	O ₁ -O ₅	O ₁ -C ₂	C ₂ -O ₃	C ₂ -C ₄	5-1-2	1-2-3	1-2-4	6-5-1-2
Conformation A								
1	1.289	1.395	1.222	1.522	117.7	119.9	112.3	109.9
2	1.295	1.384	1.212	1.596	115.9	123.8	110.2	139.9
3	1.289	1.396	1.222	1.530	117.7	119.6	111.4	110.3
4	1.288	1.396	1.219	1.529	117.2	120.4	110.8	111.7
5	1.295	1.384	1.216	1.596	116.3	122.3	111.2	139.3
6	1.295	1.384	1.213	1.590	115.9	123.3	110.2	139.2
7	1.289	1.397	1.222	1.532	117.7	119.5	111.2	110.6
8	1.289	1.397	1.222	1.532	117.7	119.5	111.2	110.5
9	1.295	1.385	1.212	1.593	115.9	123.3	109.9	138.8
10	1.295	1.385	1.212	1.593	115.9	123.3	109.9	138.9
Conformation B								
1	1.296	1.392	1.222	1.523	116.1	120.5	111.8	(180.0)
2	1.298	1.383	1.211	1.596	115.2	124.0	110.0	(180.0)
3	1.296	1.394	1.221	1.531	116.0	120.2	111.0	(180.0)
4	1.296	1.393	1.218	1.529	115.6	121.0	110.3	(180.0)
5	1.298	1.383	1.216	1.596	115.6	122.5	111.0	(180.0)
6	1.298	1.383	1.212	1.590	115.2	123.5	110.1	(180.0)
7	1.296	1.393	1.221	1.533	116.0	120.1	110.8	(180.0)
8	1.296	1.393	1.221	1.533	116.0	120.1	110.8	(180.0)
9	1.298	1.383	1.212	1.592	115.3	123.5	109.8	(180.0)
10	1.298	1.383	1.212	1.592	115.2	123.5	109.8	(180.0)

The structure for the alkyl groups in 7 and 8 was obtained simply by replacing an H atom of each CH_3 in 1 by CH_2CH_3 or $(\text{CH}_2)_5\text{CH}_3$, and the structure for 9 and 10 by replacing the F atom of 6 by CF_2CF_3 or $(\text{CF}_2)_5\text{CF}_3$. The energy optimization was carried out only for the central part of the alkanoyl peroxides. The results are shown in Table 1. As may be seen from Table 1, alkanoyl peroxides with the CH_2 group at the α position have $\theta_1=110^\circ$ and $R_{1,5}=1.289 \text{ \AA}$, while those with the CF_2 group have $\theta_1=140^\circ$ and $R_{1,5}=1.295 \text{ \AA}$. The substitution of fluorine at carbon atoms further away than the β position does not affect the molecular structure of the peroxy group.

Conformational Energy and Dihedral Angle

Figures 4 and 5 show the dependence of energy upon the dihedral angle, θ_1 , for 1, and 2. The energy increases rapidly when θ_1 becomes smaller than 90° . On the other hand, the barrier to the *trans* conformation is very small, 0.9 kcal/mol for 1 and 0.1 kcal/mol for 2. This typical θ_1 dependence of the conformational energy has been observed in benzoyl peroxide[4] and may be characteristic of diacyl peroxides. Alkanoyl peroxides can be said to rotate freely around the O-O bond between $\theta_1=180^\circ-40^\circ$ and $180^\circ+40^\circ$.

Conformation Appropriate for Bond Dissociation

In Figs. 4 and 5, the two-atom energy between the peroxy oxygen atoms, $E_{1,5}$, is also shown. When θ_1 becomes larger than 90° , $E_{1,5}$ increases, and becomes unstable by $8 \sim 9$ kcal/mol at $\theta_1=180^\circ$. This destabilization is very large as compared with that of the total energy. Thus alkanoyl peroxides take the conformation having the weak O-O bond of $\theta_1=180^\circ$ without an appreciable change in the total energy. The O-O bond cleavage can proceed through this conformation.

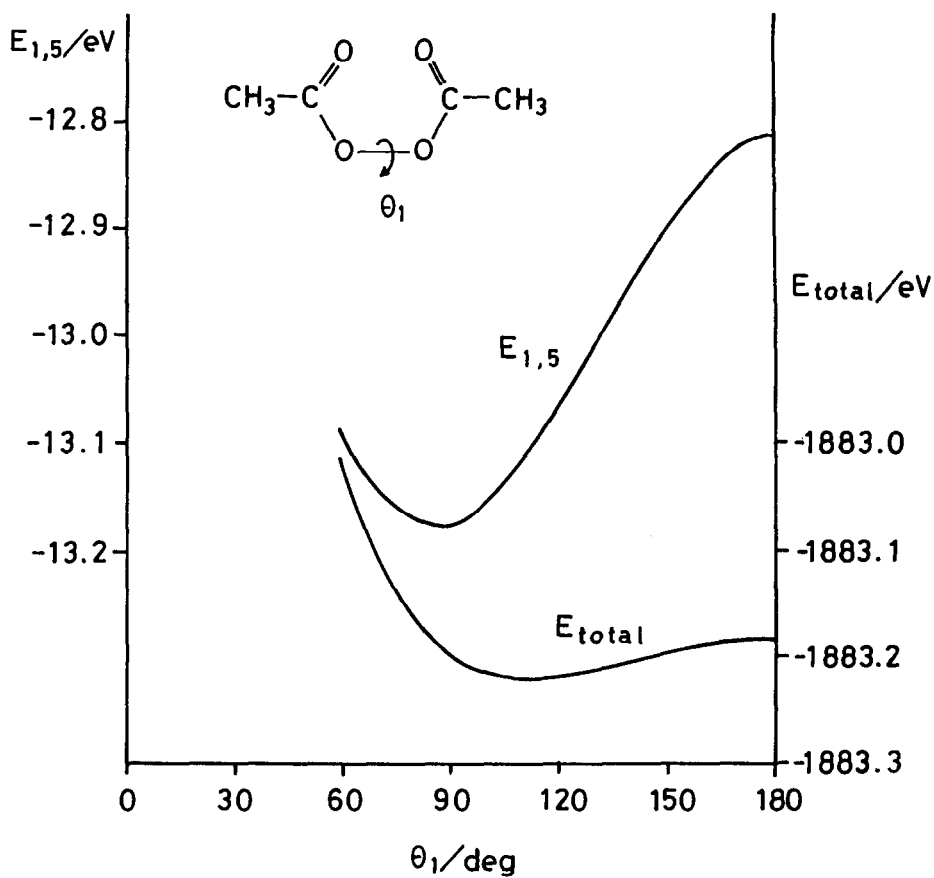


Fig.4. Dependence of total energy and two-atom energy between peroxy oxygen atoms of diacetyl peroxide, 1, upon the dihedral angle between two COO planes.

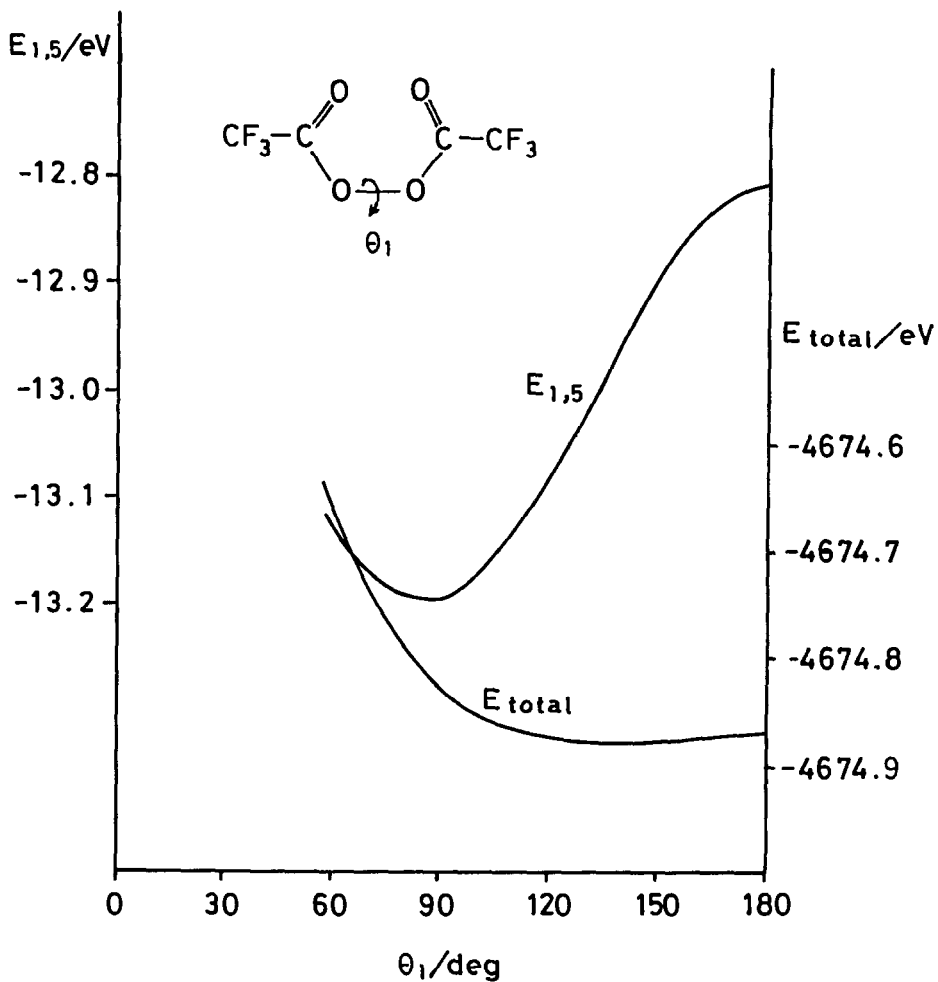


Fig.5. Dependence of total energy and two-atom energy between peroxy oxygen atoms of hexafluoroacetyl peroxide, 2, upon the dihedral angle between two COO planes.

This *trans* conformation is denoted by 'B conformation' or the 'O-O bond breaking conformation'.

ELECTRONIC STRUCTURE

Charge Distribution

Charge distribution in the B conformation is shown in Table 2. The fluorine atom at the α carbon atom has negative charge of -0.2. This induces the large positive charge at the α carbon atom, and reduces the electron density of the oxygen atoms; 0.03 electrons for the carbonyl oxygen and 0.012 electrons for the peroxy oxygen by each fluorine atom. The effect of the fluorine atom at the β carbon atom on the charge density of the oxygen atoms is half of that of the fluorine atom at the α carbon atom. The experiment has shown [6,7] that the rate of decomposition of 6 is faster than 2, while the magnitude of negative charge at the peroxy oxygen atom is smaller in 6 than in 2. Thus "the O_1-O_5 electrostatic repulsion promotes the bond cleavage" is not an appropriate explanation for fluorinated alkanoyl peroxides. Similarly, the electrostatic repulsion between O_3 and O_7 carbonyl oxygen atoms is not important for the decomposition.

Orbital Energy

Figure 6 shows two higher occupied MOs and three lower unoccupied MO's for 1, 2, 3 and 6 in their B conformations. The highest occupied MO (HOMO) of these compounds is the nonbonding-type orbital of the carbonyl oxygen atom, $n(C=O)$. In 1 and 3, two lowest unoccupied MOs are π^* orbitals, and the $\sigma^*(O-O)$ orbital lies 0.8 eV higher than these π^* orbitals. The fluorination lowers both the occupied and unoccupied

TABLE 2

Charge density of alkanoyl peroxides, $(RCOO)_2$, in the B conformation

Compound	O ₁	C ₂	O ₃	C ₄	H ₁₀	F ₁₀
1, R=CH ₃	-0.1619	0.3238	-0.3018	0.0431	0.0328	-
3, R=CH ₂ CH ₃	-0.1625	0.3330	-0.3022	-0.0020	0.0402	-
7, R=(CH ₂) ₂ CH ₃	-0.1628	0.3313	-0.3021	0.0128	0.0396	-
8, R=(CH ₂) ₆ CH ₃	-0.1627	0.3313	-0.3025	0.0099	0.0395	-
4, R=CH ₂ CF ₃	-0.1519	0.3327	-0.2616	-0.0176	0.0811	-
2, R=CF ₃	-0.1264	0.3045	-0.2056	0.6393	-	-0.2016
6, R=CF ₂ CF ₃	-0.1222	0.3065	-0.2130	0.4106	-	-0.1865
9, R=(CF ₂) ₂ CF ₃	-0.1224	0.3081	-0.2111	0.4116	-	-0.1869
10, R=(CF ₂) ₆ CF ₃	-0.1217	0.3085	-0.2103	0.4105	-	-0.1863
5, R=CF ₂ CH ₃	-0.1315	0.2962	-0.2567	0.4125	-	-0.2185

orbitals. The $\sigma^*(O-O)$ orbital is lowered remarkably, and becomes the lowest unoccupied MO (LUMO) in 6. The orbital energies of LUMO and the $\sigma^*(O-O)$ orbital are listed in Table 3. Since the $\sigma^*(O-O)$ orbital is lowered by the fluorination at the α carbon atom, the rate of the induced decomposition with benzene, which is considered to be initiated by electron transfer from benzene to the $\sigma^*(O-O)$ orbital, will be accelerated by the fluorination.

Two-Atom Energy

Table 4 shows the two-atom energy and its component energies for the O₁-O₅ and C₂-C₄ bonds. Two-atom energy between the peroxy oxygen atoms, E_{1,5}, in the α -fluorinated alkanoyl peroxides is

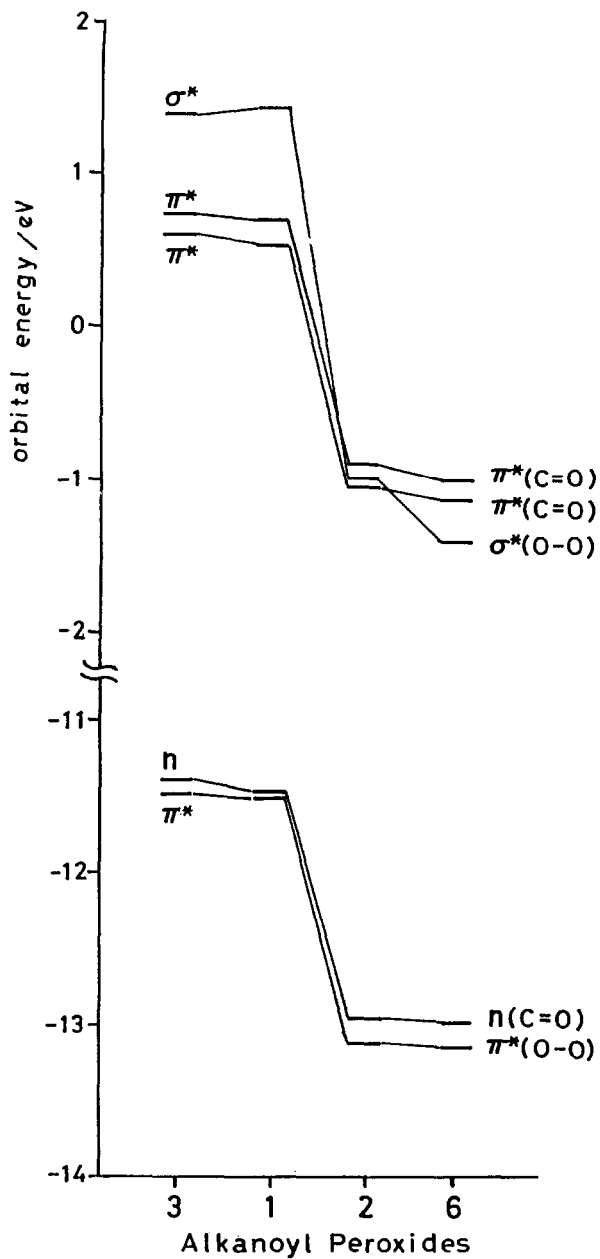


Fig.6. Energy levels of two higher occupied MOs and three lower unoccupied MOs for four alkanoyl peroxides, 1, 2, 3 and 6.

TABLE 3

Rate of decomposition (in sec^{-1}) and some electronic properties (in eV) of alkanoyl peroxides, $(\text{RCOO})_2$, in the B conformation

Compound	$k_d (\text{s}^{-1}) \times 10^8$ (25°C)	E_{1-5}^R	E_{2-4}^R	E_{1-10}	ϵ_{LUMO}	$\epsilon(\sigma^*(\text{O}-\text{O}))$
5, $\text{R}=\text{CF}_2\text{CH}_3$	96000 ^a	-17.953	-12.682	0.186	-0.198	0.121
10, $\text{R}=(\text{CF}_2)_6\text{CF}_3$	5860 ^b	-17.962	-12.821	0.155	-1.963	-1.963
9, $\text{R}=(\text{CF}_2)_2\text{CF}_3$	3320 ^c	-17.965	-12.833	0.156	-1.614	-1.614
6, $\text{R}=\text{CF}_2\text{CF}_3$	1160 ^d	-17.980	-12.885	0.152	-1.385	-1.385
2, $\text{R}=\text{CF}_3$	100 ^b	-17.996	-12.881	0.159	-1.038	-0.978
8, $\text{R}=(\text{CH}_2)_6\text{CH}_3$	6 ^e	-18.112	-14.122	0.024	0.618	1.390
7, $\text{R}=(\text{CH}_2)_2\text{CH}_3$	4 ^f	-18.111	-14.122	0.023	0.612	1.387
3, $\text{R}=\text{CH}_2\text{CH}_3$	3 ^e	-18.096	-14.183	0.022	0.592	1.393
1, $\text{R}=\text{CH}_3$	2 ^e	-18.087	-14.351	0.019	0.539	1.438
4, $\text{R}=\text{CH}_2\text{CF}_3$	1 ^g	-18.113	-14.275	-0.011	-0.375	0.062

^a Ref. 8. ^b Ref. 6. ^c Ref. 9. ^d Ref. 7. ^e Ref. 10. ^f Ref. 11. ^g Ref. 12.

larger than the corresponding nonfluorinated alkanoyl peroxides, indicating that the substitution of the fluorine atom at the α carbon atom weakens the peroxy O-O bond. This trend is observed more clearly in the $\text{C}_2\text{-C}_4$ energy; $E_{2,4}$ is -12.7 eV for the α -fluorinated alkanoyl peroxides and -14.7 eV for the nonfluorinated ones.

REACTIVITY OF O-O CLEAVAGE

Reactivity of 1 and 2

The two-atom energy between O_1 and O_5 atoms indicates that the $\text{O}_1\text{-O}_5$ bond of 2 is slightly weaker than 1. This is parallel to the

TABLE 4

Heat of formation (in kcal/mol) and two-center energy and its energy components between the O_1-O_5 and C_2-C_4 bonds (in eV) of fluorinated alkanoyl peroxides

Compound	heat of formation	E_{1-5}	E_{1-5}^R	E_{1-5}^{ES}	E_{1-5}^K	E_{2-4}	E_{2-4}^R	E_{2-4}^{ES}	E_{2-4}^K
Conformation A									
1	-110.2	-13.116	-18.608	11.108	-5.617	-14.741	-14.376	4.846	-5.212
2	-378.6	-12.947	-18.236	10.853	-5.564	-12.408	-12.875	4.987	-4.521
3	-119.3	-13.124	-18.623	11.119	-5.620	-14.718	-14.192	4.630	-5.156
4	-396.6	-13.187	-18.687	11.138	-5.638	-14.874	-14.287	4.605	-5.191
5	-283.5	-12.898	-18.199	10.847	-5.546	-12.728	-12.674	4.535	-4.589
6	-552.5	-12.937	-18.215	10.836	-5.559	-12.833	-12.877	4.632	-4.589
7	-128.4	-13.127	-18.630	11.125	-5.621	-14.663	-14.152	4.637	-5.148
8	-159.7	-13.126	-18.630	11.124	-5.621	-14.667	-14.150	4.631	-5.148
9	-721.8	-12.947	-18.235	10.851	-5.562	-12.780	-12.811	4.606	-4.575
10	-1394.5	-12.948	-18.238	10.853	-5.563	-12.773	-12.803	4.601	-4.572
Conformation B									
1	-109.3	-12.816	-18.087	10.811	-5.540	-14.723	-14.351	4.833	-5.204
2	-378.5	-12.803	-17.996	10.721	-5.529	-12.389	-12.881	5.013	-4.521
3	-118.4	-12.822	-18.096	10.817	-5.543	-14.712	-14.183	4.622	-5.151
4	-395.8	-12.862	-18.113	10.806	-5.555	-14.864	-14.275	4.595	-5.183
5	-283.4	-12.755	-17.953	10.708	-5.510	-12.720	-12.682	4.552	-4.590
6	-552.3	-12.793	-17.980	10.711	-5.524	-12.824	-12.885	4.650	-4.590
7	-127.5	-12.826	-18.111	10.829	-5.544	-14.643	-14.122	4.618	-5.139
8	-158.8	-12.826	-18.112	10.830	-5.544	-14.648	-14.122	4.613	-5.139
9	-721.6	-12.788	-17.965	10.699	-5.522	-12.776	-12.833	4.634	-4.577
10	-1394.3	-12.788	-17.962	10.697	-5.522	-12.769	-12.821	4.627	-4.574

observed rate of decomposition[6] which is faster in 2 than in 1.

The analysis of the energy components of the two-atom energy has shown that the destabilization of the O_1-O_5 bond caused by the CF_3 group is due to the decrease of the covalency and not due to the

increase of the electrostatic repulsion between O_1 and O_5 atoms. The C_2-C_4 two-atom energy differs largely between 1 and 2. The CF_3 group weakens the C_2-C_4 bond considerably, and this also may contribute to the faster rate of decomposition observed in 2.

Reactivity of 2 and 6

The comparison of 2 and 6 makes clear the effect of the fluorine atoms at the β carbon atom. The $E_{1,5}$ values indicate that the introduction of fluorine atoms at the β position makes the O_1-O_5 bond weak slightly; the analysis of the energy components has shown that the destabilization of $E_{1,5}^R$ term increases the rate of decomposition. The C_2-C_4 of 6 is stronger than 2 and the feasibility of the C_2-C_4 bond-breaking is not the reason of the faster rate of decomposition of 6 as compared with 2.

Reactivity of 9 and 10

Experiment has shown that the increase of the number of the CF_2 groups in the alkyl group increases the rate of decomposition[6]. This trend is observed in the calculated $E_{1,5}^R$ energy in the β conformation. The $E_{2,4}$ energy for 10, 9 and 6 are unstable in this order. The fluorination at the carbon atom further away than the β position makes the C_2-C_4 bond weak, which may accelerate the decarboxylation and the $O-O$ cleavage.

Reactivity of 4 and 5

The general trend expected from the calculation is that the introduction of fluorine atoms at the α and/or β positions

accelerates the rate of decomposition. Thus it is strange that the decomposition rate of 4 is slower than 3 and the rate of 5 is faster than 6. Although the $E_{1,5}^R$, $E_{1,5}$ and $E_{2,4}$ values in Table 4 reflect correctly these experimental facts, it is not easily understood why the O-O bond is strongest in 4 and weakest in 5.

The two-atom energy of 4 is compared with the nonfluorinated compounds, 1, 3, 7 and 8. The charge of the H_{10} atom of 4 is larger than those of the nonfluorinated compounds. This large positive charge stabilizes the electrostatic interaction between O_1 and H_{10} atoms as is shown in Table 5. The highest reactivity of 5 can also be understood by the same interaction. The charge of the F_{10} atom is -0.22 for 5, while those for 2, 6, 9 and 10 are -0.10 ~ -0.20, indicating that the large electrostatic repulsion between O_1 and F_{10} in 5 accelerates the O-O bond cleavage. The electrostatic repulsion between O_3 and O_5 atoms is also parallel to the observed reactivity of 4 and 5.

Induced Decomposition

The effect of fluorination has been observed clearly in the induced decomposition; the rate of decomposition induced by benzene is in the order of $2 < 9 < 10$ [6]. The induced decomposition is considered to be initiated by electron transfer from benzene to the unoccupied $\sigma^*(O-O)$ orbital. The calculated orbital energies of the $\sigma^*(O-O)$ orbital of 2, 9, and 10 are -0.98, -1.61, and -1.96 eV, respectively (Table 3). Since the lower unoccupied MO can accept an electron more easily, these values elucidate well the observed rate of the induced decomposition of perfluoroalkanoyl peroxides.

TABLE 5

Some two-atom energies (in eV) of alkanoyl peroxides

Compound	E_{1-10}	E_{3-5}	E_{3-5}^{ES}
1	0.019	0.374	0.392
3	0.022	0.380	0.397
7	0.023	0.380	0.398
8	0.024	0.381	0.398
4	-0.011	0.326	0.342
2	0.159	0.237	0.251
6	0.152	0.242	0.256
9	0.156	0.241	0.254
10	0.155	0.241	0.254
5	0.186	0.288	0.304

CONCLUSION

One of the most important findings of the present study is that the O_1-O_5 and C_2-C_4 bonds of perfluoroalkanoyl peroxides are much weaker than the corresponding nonfluorinated alkanoyl peroxides. This is reflected in the calculated two-atom energies. The introduction of the fluorine atom at the α and β positions weakens the O_1-O_5 peroxy bond. This is due to the decrease of the covalency of the O-O bond and not due to the increase of the electrostatic repulsion between O-O atoms. Very high reactivity observed for $(CH_3CF_2COO)_2$ is attributed to the large repulsion between the peroxy oxygen atom and the fluorine atom, while very

low reactivity of $(CF_3CH_2COO)_2$ to the attractive interaction between the peroxy oxygen atom and the hydrogen atom. The orbital energy of the unoccupied $\sigma^*(O-O)$ orbital correlates well with the observed rate of the induced decomposition of perfluoroalkanoyl peroxides with benzene. This indicates that the induced decomposition is initiated by electron transfer to the $\sigma^*(O-O)$ orbital.

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