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A Theoretical Study of the Possible Interaction between Sulfonium Salts and Molecular Oxygen

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The interaction between sulfonium salts and molecular oxygen was studied by the ASMO SCF method. Firstly, the results of the ASMO SCF calculation of trimethylsulfonium chloride suggested that the bond between the sulfonium cation and the anion was constituted mainly of the bonding $(d\text{-}p)\pi$-type overlaps (made by $3d_{yz}$-(or $3d_{xz}$-) of S and $3p_y$ (or $3p_x$) of Cl) and of the antibonding $(d\text{-}p)\sigma$-type overlaps (made by $3d_{z^2}$ (or $3p_z$) of S and $3p_z$ (or $3d_{z^2}$) of Cl). Secondly, the sulfonium salt interacts with molecular oxygen mainly through a $(d\text{-}p)$ σ-type overlap between the $3d_{yz}$-(or $3d_{xz}$-)orbital of the former and the $(1\pi_g)_z$-orbital of the latter. Thirdly, a maximum overlap formed between $3d$-sulfur orbitals and $1\pi_g$-orbitals of O_2 is established at the O_2-rotation angle of $\pi/4$ to the direction of the d-orbital expansion. Finally, the change in the energy state of O_2 caused by the sulfonium-salt interaction was discussed.

Some theoretical investigations into the interaction of oxygen with various organic or inorganic compounds have been made: a donor-acceptor interaction with organic solvents by Hoijtink[1] and by others[2,3] (experimentally by Evans,[4-8] Tsubomura *et al.*,[2,9] and many other authors[10-15]) with pottasium chloride by Känzig,[16] and with iodides;[17] moreover, Khan and Kearns[18] calculated the energy of the interaction of molecular oxygen with organic molecules. These studies are characterized by discussions based on the donor-acceptor interaction.

From our own previous work[19] on the catalytic nature of sulfonium salt based on the interaction with molecular oxygen, it was suggested that the "partially-occupied" d-orbitals on the central sulfur of the sulfonium ion might interact with $1\pi_g$-orbitals of the oxygen molecule and that the interaction might be possible through the orbital symmetries between the d_{yz} (or d_{xz})-sulfur orbitals and the $(1\pi_g)_z$-orbital of the oxygen molecule (a strong $(d\text{-}p)\sigma$ type) and between d_{xy} and $(1\pi_g)_x$ (a weak $(d\text{-}p)\pi$ type). Moreover, from the ultraviolet spectroscopic study[20] of the interaction between the sulfonium salts and molecular oxygen, it was found that the characteristic band near 200 mμ should not be assigned to the charge-transfer bands, but to the transition from the nonbonding $3p_z$ lone pair-orbital on the central sulfur to the $3d$-sulfur orbitals. Moreover, it was found that the molecular oxygen interacting with the sulfonium salt shifted the band to the longer wavelength in the energy region of *ca.* 0.05—0.25 eV.

It is of interest to investigate further the interaction of sulfonium salts with molecular oxygen from a theoretical point of view. The present theoretical study intends to clarify the following: a) the nature of the bond[19] between the sulfonium cation and the counter anion; b) the configuration of the mode of interaction between the sulfonium and molecular oxygen, and c) the chemical property of the oxygen molecule "activated" through the interaction with the sulfonium salts. A zero-differerential-overlap approximated ASMO SCF method including the d-orbitals of sulfur was employed for the investigations of these three features.

Method of Calculation

For the sake of mathematical convenience, a zero-differential-overlap approximated ASMO SCF method was used for the calculations of trimethylsulfonium chloride, by itself and also in interaction with oxygen.

For the calculations, the values of the orbital exponents of H, C, O, S, and Cl were supplied from the data of Clementi;[21] the ionization potentials and electron affinities of the above atoms were chosen from the values calculated by Jaffé,[22] while the values of the effective nuclear charge and the ionization potential of $3d$-sulfur orbitals were taken from Levison and Perkins.[23] These values are listed in Table 1. For one-center exchange repulsion integrals, the values of the Frank-

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Condon parameters calculated by Hinze and Jaffé[24] were used, while for one-center coulomb repulsion integrals, the Pariser approximation[25] was used, as usual. For two-center coulomb repulsion integrals, the Ohno approximation[26] was employed.

TABLE 1. PARAMETERS USED FOR THE CALCULATION

Atom	Orbital	Orbital exponent	Ionization potential (eV)	Electron affinity (eV)
S	3*s*	2.1223	20.08	11.54
	3*p*	1.8273	13.32	3.50
	3*d*	1.00	3.06	1.63
C	2*s*	1.6083	21.01	8.91
	2*p*	1.5679	11.27	0.34
H	1*s*	1.00	13.60	0.75
Cl	3*s*	2.3561	24.02	14.45
	3*p*	2.0387	13.39	3.73
O	2*s*	2.2458	36.07	18.44
	2*p*	2.2266	18.53	3.40

For the assumed configuration of the sulfonium salt, a D_3 propeller-like configuration is most plausible, as was discussed in our previous report.[19] The bond distances and angles were set up as follows: S–C=1.82 Å, C–H=1.10 Å, S–Cl=2.5—4.5 Å and $\angle$HCH=109°28′, $\angle$CSC=120°, $\angle$CSCl=90°. The geometry used for the ASMO SCF calculation is illustrated in Fig. 1.

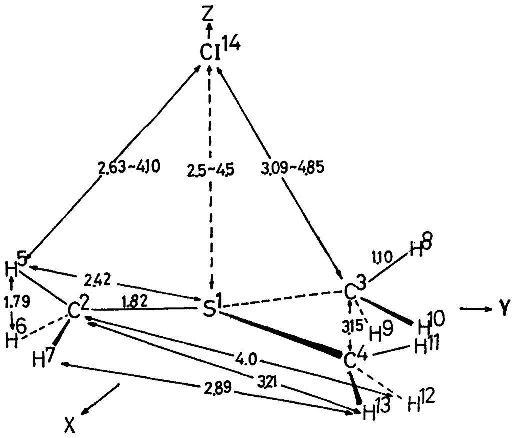

Fig. 1. Geometry used for the calculation.

Results and Discussion

Contributions of d-*Sulfur Orbitals to the Electronic State of Sulfonium Salt. Atom Population and Bond Population, Total Energy and Dipole Moment.* In order to estimate the contribution of *d*-sulfur orbitals to the S–Cl bond, an ASMO SCF calculation of trimethylsulfonium chloride was carried out both with and without inclusion of the *d*-sulfur orbitals with respect to the S–Cl distance of 2.5—4.5Å. The atom population, total energy, and dipole moment are shown in Fig. 2. As is shown in Fig. 2, in the case including *d*-sulfur orbitals, the contribution of *d*-orbitals may be reflected by the results of the smaller atom population of Cl and the significant amounts of the charge density at the *d*-orbitals of sulfur. Moreover, the charge of the C-atoms of methyl substituents becomes larger through *d*-*π* conjugation.[27] The *d*-*π* conjugation between the sulfonium cation and the counter chloride anion is directly related to the covalent nature of the S–Cl bond, as has been discussed previously.[19] On the other hand, the minimum total energy at the S–Cl distance of 3.5Å in the assumed configurations of the sulfonium chloride suggests the ionic molecular structure of the salt, considering the van der Waals radii of S (1.85 Å) and Cl (1.80Å).

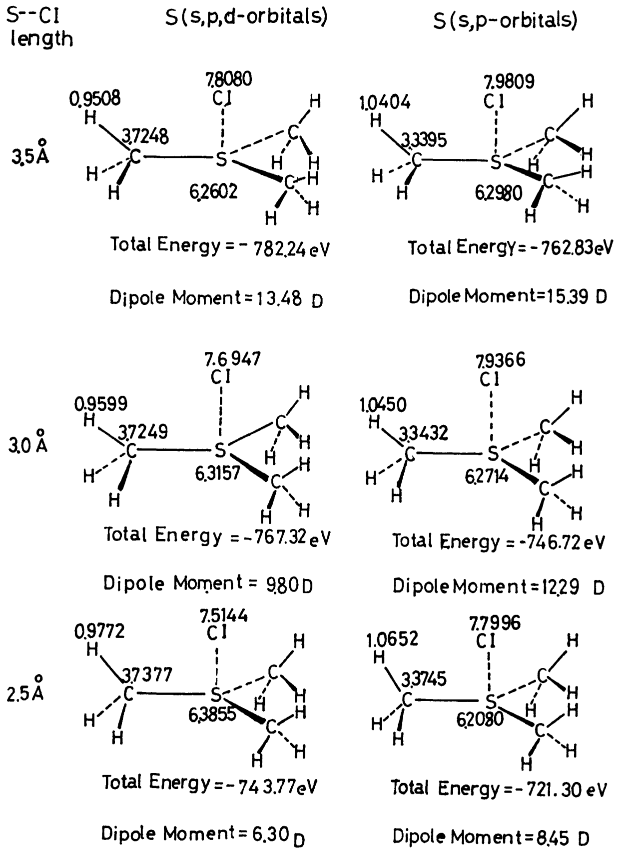

Fig. 2. The atomic propulation of $(CH_3)_3SCl$.

The Property of the Bond between the Sulfonium Cation and the Anion. It is well known that the orbital overlapping between atoms gives some idea of the aspects of the bond nature.

The bond property of S–Cl was, then, investigated from the viewpoint of the orbital overlappings in the coulomb and van der Waals distances of S–Cl (2.0 and 3.65 Å respectively). In this case, the contribution of the *s*-orbitals of both atoms to the bond formation can be neglected. The modes of the orbital overlappings of various orbitals are shown in Fig. 3. The overlap

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[27] In the case of triphenylsulfonium tetrafluoroborate, the *d*-*π* conjugation between the *d*-sulfur orbitals of the central sulfur atom and the *π*-orbitals of phenyl substituents was reflected by the red shift of the ^1L_b transition of the sulfonium in the order of 0.27 eV, as compared with the ^1L_b transition of triphenylcarbonium tetrafluoroborate, as established ultraviolet spectroscopic study (K. Ohkubo and T. Yamabe, *Bull. Japan Petr. Inst.*, **12**, 130 (1970)).

between the *d*-orbitals of sulfur and those of chlorine does not participate dominantly in the bond formation, even though a suitable maximum overlap appears in the 2.5—4.5 Å region of S-Cl, because of the vacancy of the *d*-orbitals on both atoms. The bond formation can, then, be considered to be mainly dependent on the $(d\text{-}p)\sigma$ and $(d\text{-}p)\pi$ overlaps, because the contribution of the $p\sigma$ and $p\pi$ overlaps is not so dominant in the separation beyond the distance of 3 Å. Therefore, the atomic orbital populations of both atoms and the bond orders between the atoms exhibit the bond natures characteristic of the $(d\text{-}p)\pi$ bonding orbital between the d_{xz} (or d_{yz}) of sulfur and the p_x (or p_y) of chloride and the $(d\text{-}p)\sigma$ antibonding orbital between d_{z^2} (or p_z) of S and p_z (or d_{z^2}) of Cl (see Table 2).

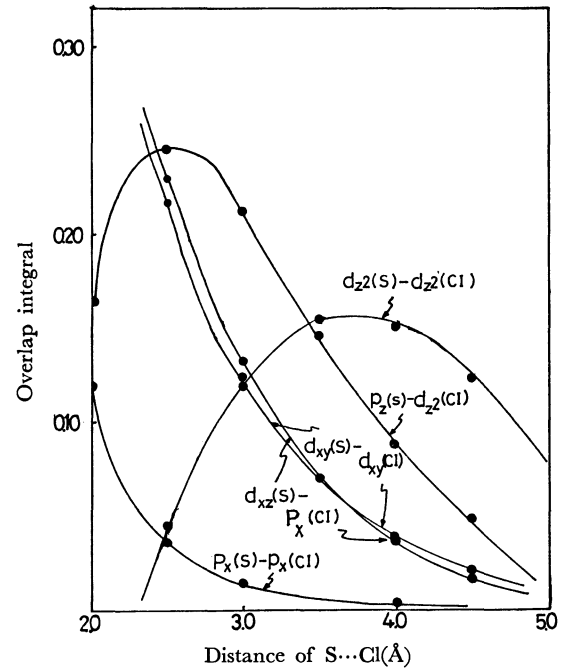

Fig. 3. Orbital overlaps between the orbitals of the central sulfur and those of the chloride.

From Table 2, the decrease in the distance of S-Cl promotes the charge transfer, as is shown in the following schemes:

Electron migration through the π-bonding orbital:

$$p_x^{(\mathrm{Cl})}(\text{or } p_y^{(\mathrm{Cl})}) \xrightarrow{\text{through } d_{xz}^{(\mathrm{S})}-p_x^{(\mathrm{Cl})} \text{ or } d_{yz}^{(\mathrm{S})}-p_y^{(\mathrm{Cl})}} d_{xz}^{(\mathrm{S})}(\text{or } d_{yz}^{(\mathrm{S})})$$

The electrons of $p_x^{(\mathrm{Cl})}$ which migrate to d_{xz} (or d_{yz}) push out the electrons of $p_x^{(\mathrm{S})}$ (or $p_y^{(\mathrm{S})}$) to $p_x^{(\mathrm{Cl})}$ (or $p_y^{(\mathrm{Cl})}$):

$$p_x^{(\mathrm{S})}(\text{or } p_y^{(\mathrm{S})}) \xrightarrow{\text{through } p_x^{(\mathrm{S})}-p_x^{(\mathrm{Cl})}} p_x^{(\mathrm{Cl})}(\text{or } p_y^{(\mathrm{Cl})})$$

Electron migration through the σ-antibonding orbital:

$$p_z^{(\mathrm{Cl})} \xrightarrow{\text{through } d_{z^2}^{(\mathrm{S})}-p_z^{(\mathrm{Cl})}} d_{z^2}^{(\mathrm{S})}$$

The electron of $p_z^{(\mathrm{Cl})}$ which has migrated to $d_{z^2}^{(\mathrm{S})}$ repulses the electrons of $p_z^{(\mathrm{S})}$, thus promoting the migration of the electrons of $p_z^{(\mathrm{S})}$ to $p_z^{(\mathrm{Cl})}$ or $d_{z^2}^{(\mathrm{S})}$.

$$\begin{tikzcd} p_z^{(\mathrm{S})} \arrow[r, "\text{through } p_z^{(\mathrm{S})}-p_z^{(\mathrm{Cl})}"] \arrow[dr] & p_z^{(\mathrm{Cl})} \\ & d_{z^2}^{(\mathrm{S})} \end{tikzcd}$$

TABLE 2. THE BOND NATURE OF S–Cl OF TRIMETHYLSULFONIUM CHLORIDE

Distance of S–Cl	AO population of S				AO population of Cl	
	$p_x=p_y$	p_z	$d_{xz}=d_{yz}$	d_{z^2}	$p_x=p_y$	p_z
4.5	1.2201	1.9290	0.0425	0.0673	1.9956	1.9447
3.5	1.1997	1.9249	0.0621	0.1413	1.9736	1.8818
3.0	1.1840	1.9173	0.0906	0.1830	1.9416	1.8601
2.5	1.1649	1.8840	0.0812	0.2347	1.9042	1.8371

AO BOND ORDER OF S–Cl

Distance of S–Cl	$p_x^{(\mathrm{S})}-p_x^{(\mathrm{Cl})}=p_y^{(\mathrm{S})}-p_y^{(\mathrm{Cl})}$	$p_z^{(\mathrm{S})}-p_z^{(\mathrm{Cl})}$	$d_{xz}^{(\mathrm{S})}-p_x^{(\mathrm{Cl})}=d_{yz}^{(\mathrm{S})}-p_y^{(\mathrm{Cl})}$	$d_{z^2}^{(\mathrm{S})}-p_z^{(\mathrm{Cl})}$
4.5	0.0022	0.0002	0.0839	−0.2841
3.5	0.0116	−0.0093	0.2122	−0.4264
3.0	0.0279	−0.0310	0.3162	−0.4469
2.5	0.0639	−0.0843	0.4340	−0.4116

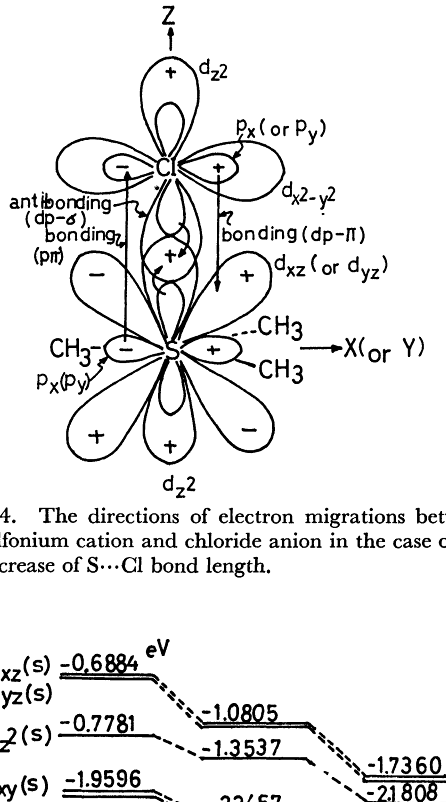

Fig. 4. The directions of electron migrations between sulfonium cation and chloride anion in the case of the decrease of S···Cl bond length.

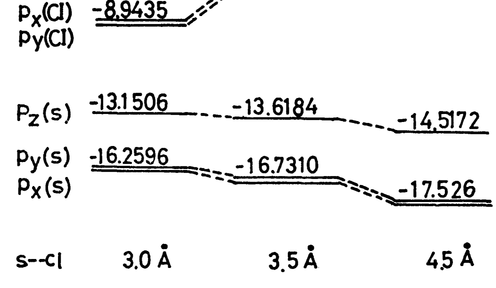

Fig. 5. An energy diagram of $(CH_3)_3SCl$.

These circumstances are illustrated in Fig. 4.

In this case, the changes in the net charges of carbon and hydrogen were very small as compared with those of sulfur and chlorine. The change in the energy levels of the *p*- and *d*-orbitals of the central sulfur and the chlorine atom with the variation in the S–Cl bond length is shown in Fig. 5.

From Fig. 5, it may be seen that, at the larger separation between S and Cl (4.5 Å), the $p_z^{(\mathrm{Cl})}$ is the highest occupied orbital and the $d_{x^2-y^2}^{(\mathrm{S})}$ is the lowest unoccupied one, while at the smaller separation (3.0 Å), the former is lowered remarkably because of the outdrawing of the charge and, as a result, the latter comes to have a partially-occupied nature, with an elevation of the energy level.

Interaction between the Sulfonium Salt and Molecular Oxygen. For the interaction between the sulfonium salt and molecular oxygen, two probable configurations can be considered as the model for the mode of interaction: One is the parallel form, and the other is the triangular one, as is shown in Fig. 6. Among the orbital overlaps between the *d*-orbitals of the central sulfur atom and the $1\pi_g$-orbitals of the oxygen molecule, a (*d*-*p*)π-type overlap or d_{yz}-$(1\pi_g)_x$ and a (*d*-π) π-type overlap of d_{xy}-$(1\pi_g)_y$ for the parallel form, and (*d*-*p*)σ-type overlaps of d_{xy}-$(1\pi_g)_x$ and d_{yz}-$(1\pi_g)_y$ for the triangular form, are possible.

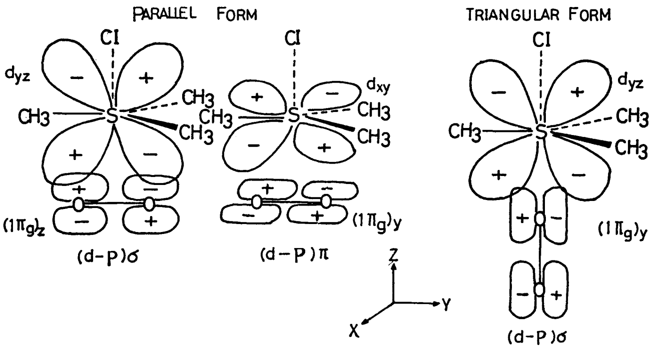

Fig. 6. Interactions between *d*-orbitals of trimenthylsulfonium chloride and $1\pi_g$-orbitals of molecular oxygen.

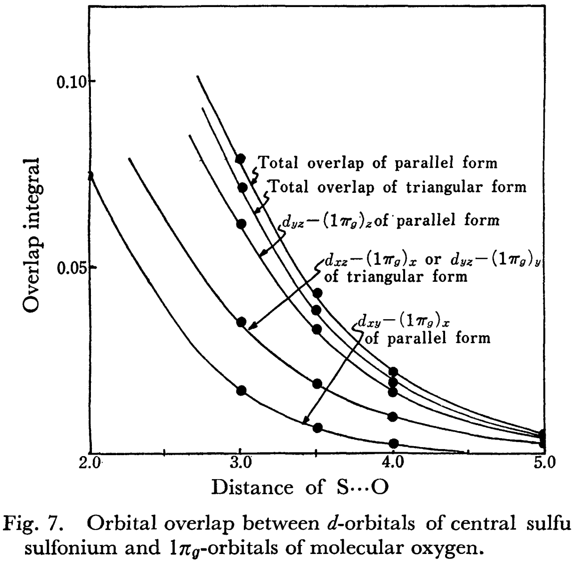

Fig. 7. Orbital overlap between *d*-orbitals of central sulfur of sulfonium and $1\pi_g$-orbitals of molecular oxygen.

The individual values of their overlap integrals were calculated. The geometry used for the mode of interaction between trimethylsulfonium chloride and the oxygen molecule is indicated in Fig. 6. As is indicated in Fig. 7, the total overlap of the parallel form is larger than that of the triangular one, and the (*d-p*)σ-type overlap is apparently larger than the (*d-p*)σ-type one; this is in agreement with the previous discussion.[19]

The Dependence of Orbital Overlaps on the Rotation around the Bond Axis between Two Oxygen Atoms. The ASMO SCF calulation was further adopted for the parallel form, in which the oxygen molecule rotates in a way parallel to the sp^2-hybrid ligand plane, as is shown briefly in Fig. 8.

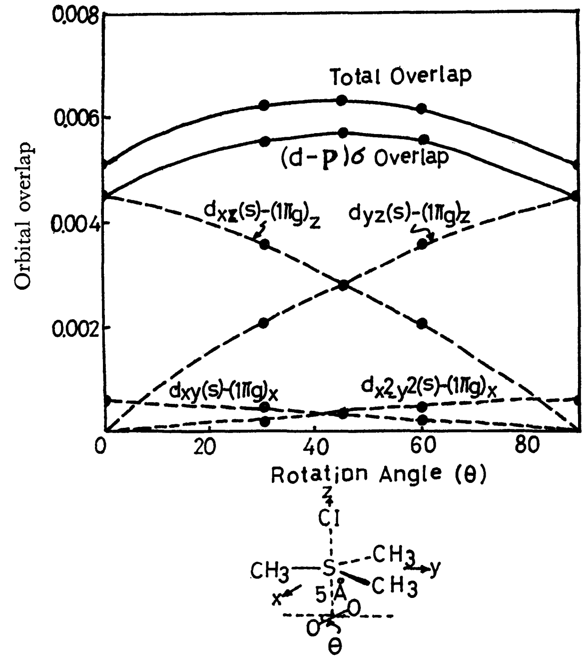

Fig. 8. Orbital overlap in case of O_2 rotation.

The dependence of the orbital overlap integrals on the rotation of the molecular axis of the oxygen molecule is indicated in Fig. 8.

Fig. 8 shows that the most preferable overlap is brought about at the rotation angle of 45° to the direction of *d*-orbital expantion. In this situation, the orbital symmetry is favorable for the formation of a methane-like bonding overlap. These circumstances are illustrated in Fig. 9. Here, it is necessary to consider the chemical nature of the oxygen molecule activated through the interaction with the sulfonium salt. When the *d*-orbitals of the central atom interact with the $1\pi_g$-orbitals of the oxygen molecule, the partially-occupied *d*-sulfur orbitals[19] (d_{yz} or d_{xz}) to which the electron flows from the counter anion may transfer the charge to the $(1\pi_g)_z$-orbital of O_2, and the $(1\pi_u)_z$-orbital electron may back-donate to the d_{z^2}-sulfur orbital. Such electron migrations promote the increase in the bond length of the oxygen molecule by the electron repulsion, and the odd-electron-charge density may localize in each oxygen atom so as to increase the radical nature of O_2. In this situation, the half-occupied, doubly-degenerated $1\pi_g$-orbitals come to be free from the de-

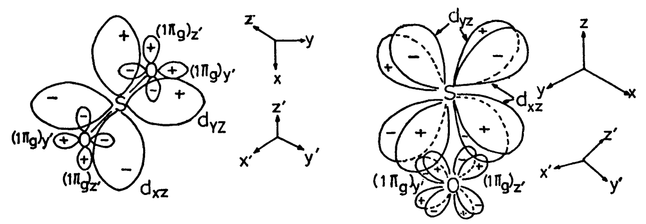

Fig. 9. An optimized interaction between sulfur *d*-orbitals and 1π-orbitals of oxygen molecule.

generated state, considering the Jahn-Teller effect.[28,29] It should be stressed here that the electron affinity and the ionization potential of the oxygen molecule are 0.15 eV[30,31] and 12.075 eV[32,33] respectively. Considering that the energy levels of the $3d$-sulfur orbitals, in particular those of d_{xz} and d_{yz}, are -0.688, -1.736 eV at the S-Cl distances between 3.0 and 3.4 Å (see Fig. 5), the energy level of -0.15 eV of the oxygen molecule might play an important role in the interaction with the $3d$-sulfur orbitals because of possibility of perturbation between them. Further work about the electronic state of the oxygen molecule calculated by means of non-empirical calculation may clarify this point.

The most suggestive results obtained from this study may be summarized as follows:

a) The bond between the sulfonium cation and the anion of the sulfonium salts is constituted mainly by the bonding $(d\text{-}\pi)\pi$-type overlaps made by the $3d_{yz}$- (or $3d_{xz}$-) sulfur orbital and the $3p_y$- (or $3p_x$-) chloride orbital and by the antibonding $(d\text{-}\pi)\sigma$-type overlaps made by the $3d_{z_2}$- (or $3p_z$-) sulfur orbital and the $3p_z$- (or $3d_{z_2}$-) chloride orbital.

b) As to the interaction between the *d*-orbitals of sulfonium salt and the $1\pi_g$-orbitals of the oxygen molecule, orbital symmetries allow two modes of interaction (the parallel form and the triangular one). The former is stronger than the latter. In the parallel form of the interaction, a $(d\text{-}p)\sigma$-type overlap is predominant over a $(d\text{-}p)\pi$-type overlap, as has been suggested previously.[19]

c) The maximum overlap of the $(d\text{-}p)\sigma$ type formed between the sulfonium salt and molecular oxygen is possible when the oxygen molecule rotates at the angle of $\pi/4$ around its bond axis parallel to the sp^2-hybrid ligand plane of the sulfonium cation.

d) The electron inflowing from the $3d$-orbitals of the sulfonium to the $1\pi_g$-orbitals of O_2 localizes the electron charge of the orbitals, which may be connected with the increase in the radical nature of O_2.

The calculations have been carried out on the FACOM 230.60 computer at the Computer Center of Kyoto University.

The authors wish to express their cordial thanks to Professor Kenichi Fukui, who made a number of valuable suggestions and commented on major portions of this study.

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33) Other data are 12.2±0.3 eV (G. L. Weissler, J. A. R. Samson, M. Ogawa, and G. R. Cook, *J. Opt. Soc. Amer.*, **49**, 338 (1959)) and 12.21±0.04 eV (D. C. Frost and C. A. McDowell, in "Advance in Mass Spectrometry," edited by J. D. Waldron, Pergamon Press, London (1959), p. 413).