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A MO-theoretical Study of the Catalytic Activity of Onium Compounds in the Liquid-phase Oxidation

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A theoretical study with the extended Hückel method augmented by *d*-orbitals was undertaken in order to elucidate the relation between the electronic structures of various onium compounds and their catalytic activities in the liquid-phase oxidation of hydrocarbons. There were several findings. Firstly, the differences in the catalytic activities of the carbonium, ammonium, and oxonium compounds are ascribed to those in the AO populations of the p_z-orbitals on their central atoms. Secondly, the distinguished activities of sulfonium and phosphonium compounds were well explained by the partially-occupied sulfur or phosphorus 3*d*-orbitals, in which the d_{xz} (or d_{yz}) orbital is utilized most effectively for the interaction with the $(1\pi_g)_z$-orbital of O_2. Finally, the relatively low activities of arsonium and telluronium compounds are ascribed to the vacant and diffused 4*d* or 5*d* orbitals, while the appreciable activity of the selenonium compound is caused by the partial electron-occupancy of the $4d_{xz}$ (or $4d_{yz}$) orbital of the central selenium.

The catalyst in the liquid-phase oxidation of hydrocarbons has been widely investigated from the viewpoints of both theory and technology. Among several oxidation catalysts, such as transition metal compounds[1] (including chelates[2] and complexes[3]) and halogen compounds[4] (involving ammonium salts[5]), ammonium salt-catalysts exhibit some especially interesting features in their catalytic behavior because they show little activity for the promotion of the oxidation reaction, even though the ammonium cation possesses the counter anion of perchlorate[5] or tetrafluoroborate,[6] and also because the difference in the substituents attached to the central nitrogen has an influence upon the catalytic activity. Our own previous studies[7,8] of the catalytic activities of several onium compounds demonstrated that the activity was affected directly by the differences in the onium central atoms and immediately by those in the structures of the counter anions and the substituents. That is, sulfonium and phosphonium salts involving the lower vacant 3*d*-orbitals (strictly speaking, the partially-occupied 3*d*-ones) were found most effective, and it was shown that the larger the alkyl group attached to the central atom, the higher the catalytic activity. As for the counter anions, phosphate, sulfate, *etc.* are more active than halides. These experimental phenomena are directly connected with the catalytic activation of molecular oxygen, as was suggested by our spectroscopic[9] and theoretical[10,11] investigations concerning the possible interaction between the catalyst and O_2.

In this paper, we will attempt to clarify the correlation between the electronic structures of onium compounds and their catalytic activities in the liquid-phase oxidation of hydrocarbons, such as cumene and α-pinene. For example, the catalytic activity of several onium tetrafluoroborates has been found to be in approximately the following order: carbonium$<$ammonium$<$oxonium, silyl$<$phosphonium$\simeq$sulfonium, arsonium$\simeq$telluronium$<$selenonium. Extended Hückel molecular orbital (EHMO) calculations were performed on these onium compounds.

Method of Calculation

The extended Hückel method (EHMO) proposed by Hoffmann[12] was adopted to the calculations of $(CH_3)_3CCl$, $(CH_3)_4NCl$, $(CH_3)_3OCl$, $(CH_3)_3SiCl$, $(CH_3)_4PCl$, $(CH_3)_3SCl$, $(CH_3)_4AsCl$, $(CH_3)_3SeCl$, and $(CH_3)_3TeCl$. Methyl derivatives of onium compounds were taken for mathematical convenience. The geometries used for the calculations are illustrated in the figures of this paper.

The orbital exponents and the Coulomb integrals ($H_{\mu\mu}$) were supplied by Clementi[13] and Jaffè,[14,15] respectively. Especially, the $H_{\mu\mu}$ value of the oxygen 2*p*-orbital was obtained from the atomic ground-state ionization potential[14] ($H_{\mu\mu}(\mathrm{O}\ 2p) = -13.61$ eV). The $H_{\mu\mu}$ values of the *d*-orbitals of S, P, As, Se, and Te were -7.00,[16] -6.53, -5.00, -4.00, and -4.00 eV respectively. The resonance integrals ($H_{\mu\nu}$) were evaluated by the Wolfsberg-Helmholtz approximation[17]:

$$H_{\mu\nu} = 0.875(H_{\mu\mu}+H_{\nu\nu})S_{\mu\nu}$$

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[1] For instance, J. A. Barnard and D. S. Mitchell, *J. Catal.*, **12**, 386 (1968); W. F. Brill, *Ind. Eng. Chem.*, **52**, 837 (1960), and the references cited therein.

[2] L. H. Vogt, Jr., *Chem. Rev.*, **63**, 269 (1963), and the references cited therein.

[3] L. Vaska, *Science*, **140**, 809 (1963); S. Otsuka, A. Nakamura, and T. Tatsuno, *Chem. Commun.*, **1967**, 836, *etc.*

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[12] R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); **40**, 2474 (1964).

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[15] J. Hinze and H. H. Jaffè, *J. Phys. Chem.*, **67**, 1501 (1963).

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[17] M. Wolfsberg and L. Helmholtz, *J. Chem. Phys.*, **20**, 837 (1952).

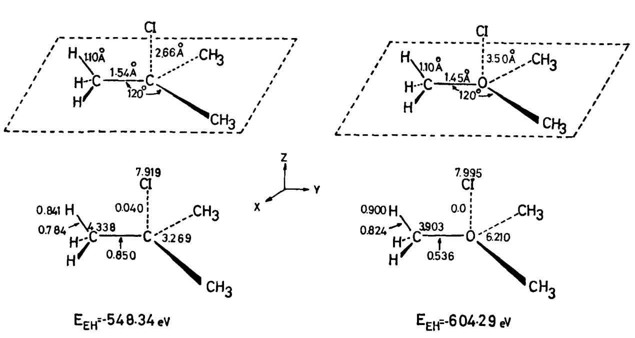

Fig. 1. Valence electron distributions and total energies of $(CH_3)_3CCl$ and $(CH_3)_3OCl$.

where $S_{\mu\nu}$ is the overlap integral between AOs.

The wave-function contours were calculated on the basis of the Slater AO functions.[18]

Results and Discussion

Electronic Structures of Second-row Onium Compounds. It is necessary at first to assume the molecular structures of carbonium, ammonium, and oxonium compounds under the present experimental conditions. In view of the propeller-like D_3 symmetry of the triphenylcarbonium cation[19] and the ionic property of these compounds, it is plausible to assume planar C_{3v} structures for the trimethylcarbonium and trimethyloxonium cations.[20] On the basis of the above discussion, the EHMO calculations were performed for $(CH_3)_3CCl$ and $(CH_3)_3OCl$ at the ionic distances of C–Cl and O–Cl (2.66 and 3.5 Å respectively). The valence-electron distributions of the above compounds are shown in Fig. 1. In regard to the structure of $(CH_3)_4NCl$, two representative configurations can be considered: one of them takes the C_{4v} symmetry of the ammonium cation, while the other takes the T_d symmetry. The two distinct electronic structures of $(CH_3)_4NCl$ are indicated in Fig. 2.

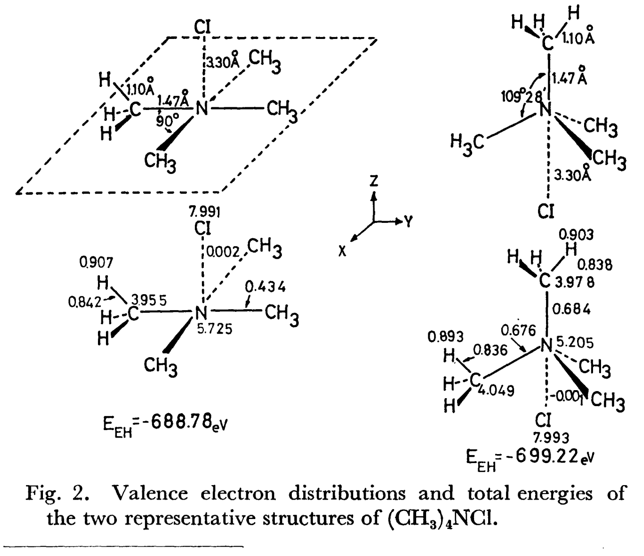

Fig. 2. Valence electron distributions and total energies of the two representative structures of $(CH_3)_4NCl$.

The catalytic activities of the second-row onium compounds were not remarkable as compared with sulfonium and phosphonium compounds. This may be ascribed to their inoic character, which reflects the small or negative overlap population between the cation and the anion (see M_{A-Cl} in Table 1), considering that the considerable covalency of the bond between the cation and the anion contributes directly to the partial electron-occupation of the lowest unoccupied (LU) central-atom orbital, which can then be utilized for the interaction with the $1\pi_g$-orbitals of O_2.

It is necessary here to discuss the order of the activity, carbonium<ammonium<oxonium, in hydrocarbon oxidations. In the case of carbonium and oxonium catalysts, the interaction between the catalyst and the $(1\pi_g)_z$-orbital of O_2 takes place in the direction of the p_z-orbital of the central atom from the opposite side of the counter anion, since, in such a mode of interaction, an overlapping of the orbitals but no steric hindrance can be expected. The above discussions lead to an assumption that the partially-occupied carbon p_z-orbital (the LU orbital of $(CH_3)_3CCl$) and the nonbonding oxygen p_z-orbital (the highest occupied (HO) orbital of $(CH_3)_3OCl$) play an important role in the interaction with the $(1\pi_g)_z$-orbital of O_2. That is, the AO population of the HO level on the p_z-orbital of the central atom $(N_{HO}(Z_A))$ is closely related to the catalytic activity, because the activity results from the electron-donor property of the onium cation.[8] In the case of the ammonium catalyst, the interaction between the p_z-orbital of the ammonium cation and the $(1\pi_g)_z$-orbital of O_2 is sterically hindered to some extent by the substituents attached to the central nitrogen. The values of $N_{HO}(Z_A)$ and the AO population of the central atom $(N(Z_A))$ are listed in Table 1. The order of the above values is in agreement with the catalytic activity as defined by the maximum reaction rate (R_{max}).

Electronic Structures of Third-row Onium Compounds. The EHMO calculations were carried out on the electronic structures of onium compounds possessing third row-atoms, *i.e.*, silyl, phosphonium, and sulfonium compounds. The silyl compound was taken as a com-

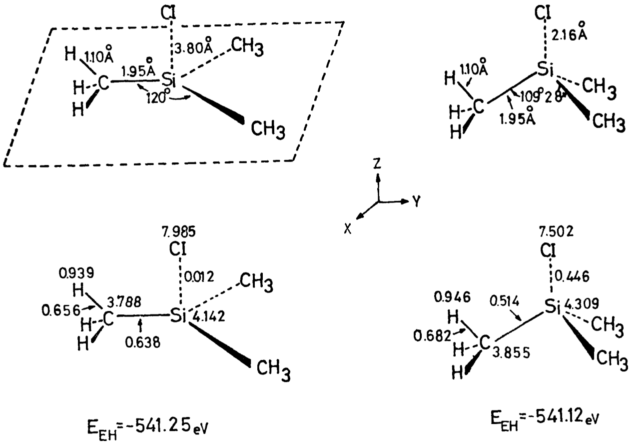

Fig. 3. Valence electron distributions and total energies of the two distinct $(CH_3)_3SiCl$.

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[18] J. C. Slater, *Phys. Rev.*, **36**, 57 (1930).

[19] D. W. A. Sharp and N. Sheppard, *J. Chem. Soc.*, **1957**, 674.

[20] The ASMO SCF calculations on $(CH_3)_3SCl$[9] have found that the planar C_{3v} symmetry of the sulfonium cation was most stable energetically. This may support the planar C_{3v} symmetry of the oxonium cation.

TABLE 1. RELATION BETWEEN THE ELECTRONIC STRUCTURES OF SECOND ROW ONIUM COMPOUNDS AND THE CATALYTIC ACTIVITIES

Onium chloride R_3ACl or R_4ACl		A–Cl (Å)	M_A[a)]	M_{A-Cl}[b)]	$N(Z_A)$[c)]	$N_{HO}(Z_A)$[c)]	Orbital energy (eV)		$R_{max} \times 10^4$[d)] (mol/l sec)	
							HO	LU		
$(CH_3)_3C$		2.66	3.27	0.039	0.296	0.0018	−12.79	−9.19	0.26[a)]	0.52[b)]
$(CH_3)_4N$	T_d	3.30	5.20	−0.001	1.267 (1.263[e)])	0.0444 (0.0[e)])	−13.11	0.45	0.34[a)]	0.74[b)]
	C_{3v}	3.30	5.73	0.002	1.957	−0.0	−10.42	−3.88		
$(CH_3)_3O$		3.50	6.201	0.0	1.981	0.357	−11.74	−1.34	0.67[a)]	0.82[b)]

a) Atom population of the central atom. b) Overlap population between the cation and the anion. c) AO populations of the p_z-orbital of the central atom and that at the HO MO ($N_{HO}(Z_A)$). d) R_{max} values were obtained from cumene (a) and α-pinene (b) oxidations at 85°C, respectively. e) Values are those of p_x and p_y.

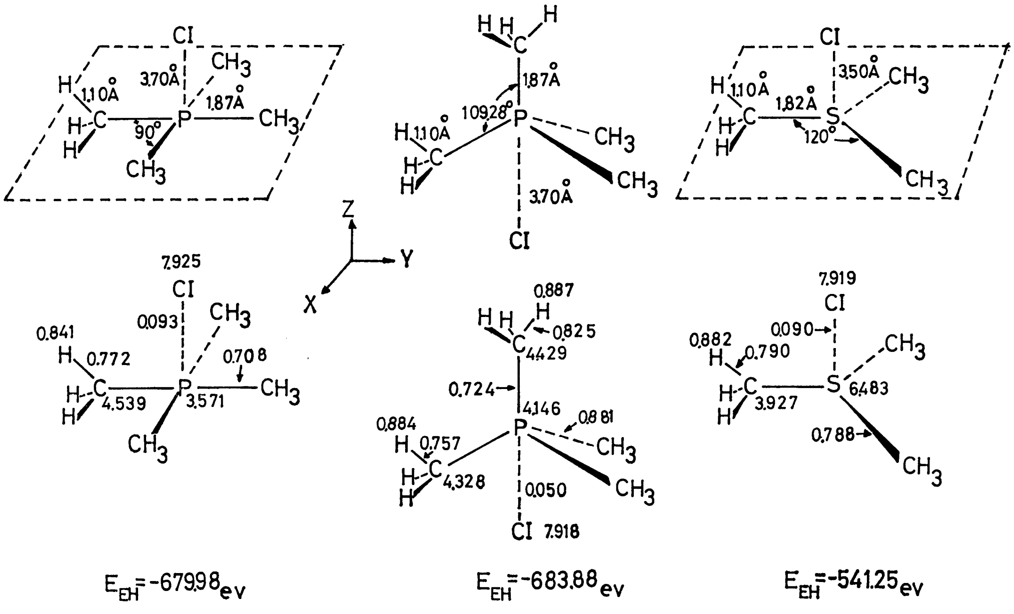

Fig. 4. Electronic structures of $(CH_3)_4PCl$ and $(CH_3)_3SCl$.

parison. As to the molecular structure of the sulfonium compound, the planar C_{3v} symmetrical sulfonium cation gave the most stable configuration of the trimethylsulfonium compounds.[20)] The structures of silyl and phosphonium compounds have, however, thus far remained obscure. There are two possible representative configurations for each of the cations, silyl and phosphonium: for the former, one is the planar C_{3v} symmetrical silyl cation and the other is the C_{3v} symmetrical silyl compound,[21)] while for the latter, the one is the C_{4v} symmetrical phosphonium ion and the other is the T_d symmetry of the phosphonium compound. Figures 3 and 4 show the configurations of these compounds and the electronic structures, together with the total energies (E_{EH}). $(CH_3)_3SiCl$ would take the C_{3v} symmetry, although the Si–Cl bond may be lengthened to some extent in hydrocarbons involving such polar oxidation

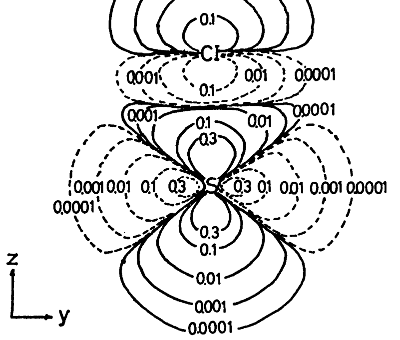

Fig. 5. Orbital contour of $(CH_3)_3SCl$ at the LU MO. (the solid and broken lines stand for the positive and the negative MO signs respectively.)

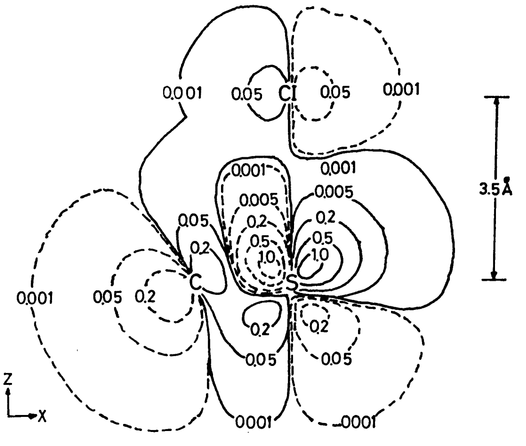

Fig. 6. Orbital contour of $(CH_3)_3SCl$ at the LU+1 MO.

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21) E. Newman, J. K. O'Loane, S. R. Polo, and M. K. Wilson, *J. Chem. Phys.*, **25**, 855 (1956).

TABLE 2. RELATION BETWEEN ELECTRONIC STRUCTURES OF THIRD ROW ONIUM COMPOUNDS AND THE CATALYTIC ACTIVITIES

Onium chloride R_3ACl or R_4ACl		A–Cl (Å)	N_A			N_d					$R_{max}\times 10^4$ (mol/l sec)
			p_z	p_y	p_x	d_{xz}	d_{yz}	d_{xy}	$d_{x^2-y^2}$	d_{z^2}	
$(CH_3)_3Si$	C_{3v}	3.80	0.161	1.410	1.411						$0.75^{b)}$
$(CH_3)_3SiCl$	C_{3v}	2.16	0.308	1.423	1.423						
$(CH_3)_4P$	C_4	3.70	0.453	0.833	0.833	0.137	0.137	0.056	−0.067	0.032	$0.89^{b)}$
	T_d	3.70	0.883	0.885	0.828	0.122	0.144	0.105	0.031	0.021	
$(CH_3)_3S$	C_{3v}	3.50	1.981	0.992	0.992	0.142	0.142	0.092	0.092	0.068	$1.12^{a)}$ $0.97^{b)}$

R_{max} indicates the maximum oxidation reaction rates in cumene (a) and α-pinene (b) at 85°C.

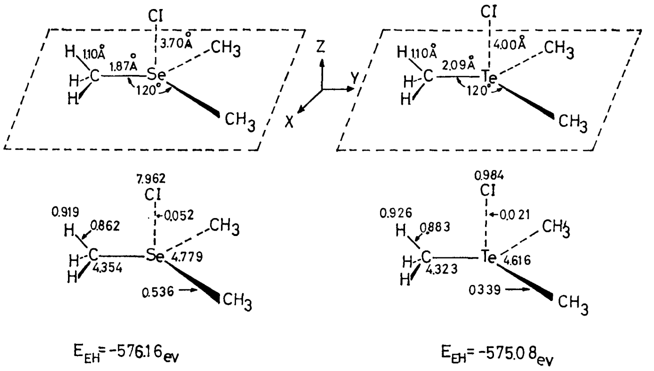

Fig. 7. Electronic structures of $(CH_3)_3SeCl$ and $(CH_3)_3TeCl$ in two distinct configurations.

products as alcohols and hydroperoxides.

Among the onium compounds utilized for the liquid-phase oxidation catalysts, phosphonium and sulfonium compounds exhibit the most remarkable activity. The extraordinary activities of these compounds are due to the catalytic activation of molecular oxygen by means of their partially occupied d-orbitals, in which the d_{xz} or the d_{yz} is the most preferable orbital for the interaction with the $(1\pi_g)_z$-orbital of O_2.[10,11] Moreover, the mode of the interaction has been discussed in detail in Refs. 8, 10, and 11. This partial occupancy of the sulfur or phsophorus d-orbitals is not only due to the somewhat covalent nature of the bond between the onium cation and the counter anion, but also to the d–π interactions between the carbon p-orbitals of the substituents and the d-orbitals. Some aspects of these features mentioned above can be explained by the orbital contours of $(CH_3)_3SCl$ illustrated in Figs. 5 and 6.

In conclusion, the order of the catalytic activity, silyl<phosphonium<sulfonium, can be well explained by the small AO population of the p_z-orbital of the silyl compound and the almost identical AO populations of the d-orbitals (indicated by N_d in Table 2) of phosphonium and sulfonium compounds. It is necessary here to mention that, in the case of the sulfonium compound, the nonbonding sulfur p_z-orbital at the HO MO may contribute to some extent to the increase in the electron-donor property of the compound, while the nonbonding or electron-rich p-orbitals can not be expected in the case of the phosphonium compound.

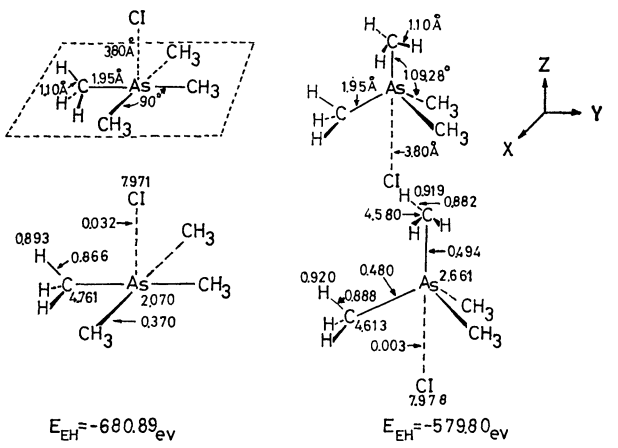

Fig. 8. Electronic structure of $(CH_3)_4AsCl$ in two distinct configurations.

Electronic Structures of Fourth- or Fifth-row Onium Compounds. The onium compounds discussed in this section are arsonium, selenonium, and telluronium compounds. In regard to the structures of selenonium and telluronium compounds, they would take the planar C_{3v} symmetrical cations much like the sulfonium compound. On the other hand, two distinct structures can be considered for the arsonium compound; one takes the C_{4v} symmetrical ligand plane of the arsonium ion, while the other takes the T_d symmetrical arsonium ion. Perhaps, the latter configuration is more plausible. The

TABLE 3. RELATION BETWEEN ELECTRONIC STRUCTURES OF FOURTH AND FIFTH ROWS ONIUM COMPOUNDS AND THE CATALYTIC ACTIVITIES

Onium Chloride R_3ACl or R_4ACl		A–Cl (Å)	N_A			N_d					$R_{max}\times 10^4$ (mol/l sec)
			p_z	p_x	p_y	d_{xz}	d_{yz}	d_{xy}	$d_{x^2-y^2}$	d_{z^2}	
$(CH_3)_4As$	C_4	3.80	0.427	0.784	0.784	−0.042	−0.042	−0.186	−0.517	−0.0647	0.22
	T_d	3.80	0.806	0.837	0.790	−0.125	−0.096	−0.119	−0.185	−0.202	
$(CH_3)_3Se$	C_{3v}	3.70	1.989	0.836	0.836	0.020	0.200	−0.111	−0.111	−0.008	1.04
$(CH_3)_3Te$	C_{3v}	4.00	1.991	0.804	0.806	−0.024	−0.024	−0.168	−0.174	−0.043	0.45

R_{max} stands for the maximum reaction rate in the cumene oxidation at 85°C.

valence electron distributions of $(CH_3)_3SeCl$, $(CH_3)_3TeCl$, and $(CH_3)_4AsCl$ are shown in Figs. 7 and 8.

The relatively low catalytic activities of these compounds as compared with sulfonium and phosphonium compounds may be attributed to the diffused 4*d* or 5*d* orbitals of the central atoms. Especially, the arsonium compound and the telluronium compound indicate negative N_d values for the AO populations of their *d*-orbitals. On the other hand, the appreciable activity of the selenonium compound results from the partial-occupied selenium d_{xz} or d_{yz} orbital. The order of the activity, arsonium$\simeq$telluronium$<$selenonium, can be well explained by that of the N_d values indicated in Table 3.

The molecular structures of the onium compounds discussed in this paper will be treated in more detail in a succeeding report.

Most of the calculations were carried out on FACOM 230.60 computer at the Computer Center of Kyushu University, but some of them were done at the Computer Center of Kyoto University.