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A Theoretical Account of the Correlation between the Electronic Properties of Onium Compounds and Their Catalytic Activities in the Liquid-phase Oxidation of Hydrocarbons

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Previous studies[1,2] have suggested that onium compounds catalyze the liquid-phase oxidation of hydrocarbons. The catalytic activity of onium compounds containing C, N, O, P, S, As, Se, and Te as their onium central atoms is directly affected by the difference in the central atoms and indirectly by that in the counteranions and the substituents attached to the central atom. The larger the alkyl groups possessing the electron-donor property employed as substituents, the higher the catalytic acitvity, while the counteranions of phosphate, sulfate, *etc.* are more active than those of halides. As has been suggested by the spectroscopic[3] and theoretical[4,5] investigations of the possible interaction between the onium compound and molecular oxygen, these experimental phenomena can be considered to be immediately related to the catalytic activation of O_2. The present theoretical study with a semiempirical ASMO SCF method and an extended Hückel method[6] including all the valence electrons in a molecule appeared significant in elucidating the correlation between the electronic properties of onium compounds and their catalytic activities in the liquid-phase oxidation of such hydrocarbons as cumene and α-pinene.[1,2] The silyl compound will also be considered in this report for the sake of comparison.

First, we will discuss the molecular geometries of onium compounds (trimethyl- or tetramethyl-onium chlorides were used) from the energetic point of view. According to the total energies of the compounds listed in Table 1, the stable geometries of the trimethyl onium chlorides (carbonium, oxonium, sulfonium, selenonium, and telluronium) were found in those taking the planar structures of onium cations, while tetramethylonium chlorides (ammonium, phosphonium, and arsonium chlorides) have cations with tetrahedral forms.

Some mention should be made here of the geometries of onium compounds. An experimental finding has

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[1] K. Fukui, K. Ohkubo, and T. Yamabe, This Bulletin, **42**, 312 (1969).

[2] K. Ohkubo and T. Yamabe, *Bull. Japan Petrol. Inst.*, **12**, 130 (1970).

[3] K. Ohkubo and T. Yamabe, *J. Org. Chem.*, **36**, 3149 (1971).

[4] K. Ohkubo and T. Yamabe, This Bulletin, **44**, 1183 (1971).

[5] K. Ohkubo, *Tetrahedron Lett.*, **1971**, 2571, 2897.

[6] C. C. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951) for the SCF MO; R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); *ibid.*, **40**, 2474 (1964) for the extended Hückel MO. The valence orbital ionization potentials (and electron affinities) of the *d*-orbitals of P, S, As, Se, and Te were taken to be 6.53 eV (0.8 eV), 7.00 eV (2.40 eV), 4.00 eV (1.0 eV), 5.00 eV (2.0 eV), and 4.00 eV (2.1 eV) respectively on the basis of the following references: H. O. Prichard and H. A. Skinner, *Chem. Rev.*, **55**, 745 (1955); *Trans. Faraday Soc.*, **49**, 1254 (1953); T. Jordan, H. W. Smith, L. L. Lohr, Jr., and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **85**, 846 (1963). Those of *s* and *p* orbitals of the atoms were cited from J. Hinze and H. H. Jaffé, *J. Amer. Chem. Soc.*, **84**, 540 (1962); *J. Chem. Phys.*, **67**, 1501 (1963). For the Coulomb repulsion integrals, $((pp|pp)$ and $(pp|qq))$, $(pp|pp)$ were estimated by the Pariser approximation (R. Pariser, *J. Chem. Phys.*, **21**, 568 (1953)), while $(pp|qq)$ was evaluated by the Ohno approximation (K. Ohno, *Theoret. Chim. Acta*, **2**, 219 (1964)). For more details on the calculation method, see H. Kato, This Bulletin, **44**, 348 (1971), *etc.*

TABLE 1. THE RELATION BETWEEN TOTAL ENERGIES OF ONIUM COMPOUNDS AND THEIR MOLECULAR GEOMETRIES

Onium compound $(CH_3)_3ACl$ or $(CH_3)_4ACl$	Structure of onium cation	A–C (Å)	A–Cl (Å)	Dipole moment (D)	Total energies (eV) EHMO	Total energies (eV) SCF MO
$(CH_3)_3CCl$	planar (C_{3v})	1.54	2.66	5.398	−548.34	−662.90
		1.54	2.00	3.308	−544.06	−617.41
		1.54	1.76[a]	2.696	−541.32	−591.46
$(CH_3)_4NCl$	planar (C_{3v})	1.47	3.30	9.483	−688.78	−699.61
	tetrahedral (T_d)	1.47	3.30	14.660	−699.22	−713.55
$(CH_3)_3OCl$	planar (C_{3v})	1.45	3.20	14.722	−604.29	−796.15
		1.45	3.00	12.850	−603.90	−782.81
		1.45	1.65[a]	4.207	−579.25	−655.21
	pyramidal (C_{3v})	1.45	1.65[a]	4.207	—	−683.03
$(CH_3)_3SiCl$	planar (C_{3v})	1.95	3.80	9.483	−541.25	−703.65
	pyramidal (C_{3v})	1.95	2.16[a]	3.124	−541.12	−659.21
$(CH_3)_4PCl$	planar (C_{4v})	1.87	3.70	6.007	−679.98	−852.00
	tetrahedral (T_d)	1.87	3.70	7.617	−683.88	−856.49
$(CH_3)_3SCl$	planar (C_{3v})	1.82	3.50	7.088	−541.25	−788.59
	pyramidal (C_{3v})	1.82	3.50	16.21	—	−769.11
$(CH_3)_4AsCl$	planar (C_{4v})	1.95	3.80	14.699	−680.89	−780.01
	tetrahedral (T_d)	1.95	3.80	13.212	−579.80	−787.44
$(CH_3)_3SeCl$	planar (C_{3v})	1.87	3.80	11.454	−576.16	−782.56
	pyramidal (C_{3v})	1.87	2.15[a]	2.97	−563.67	−728.40
$(CH_3)_3TeCl$	planar (C_{3v})	2.09	4.00	12.141	−575.08	−809.49
	pyramidal (C_{3v})	2.09	2.31[a]	5.661	−566.75	−756.49

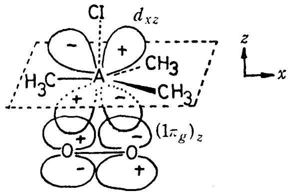
a) Covalent bond lengths. Another values of A–C bond indicate ionic distances.

TABLE 2. THE CORRELATION BETWEEN THE AO POPULATIONS OF CENTRAL-ATOM ORBITALS UTILIZED FOR THE INTERACTION WITH $1\pi_g$-ORBITALS OF O_2 AND THEIR CATALYTIC ACTIVITIES

Onium compound $(CH_3)_3ACl$ or $(CH_3)_4ACl$	Bond population A–C	Bond population A–Cl	AO population p_z	AO population d_{xz}	AO population d_{xy}	$R_{max}\times 10^4$ [a] (mol/*l* sec)
$(CH_3)_3CCl$	0.850	0.040	0.596	—	—	0.26 (0.52)
$(CH_3)_4NCl$	0.676	−0.001	1.235	—	—	0.34 (0.74)
$(CH_3)_3OCl$	0.536	0.000	1.939	—	—	0.67 (0.82)
$(CH_3)_3SiCl$	0.638	0.012	0.495	—	—	(0.75)
$(CH_3)_4PCl$	0.881	0.050	0.996	0.258	0.241	(0.89)
$(CH_3)_3SCl$	0.788	0.090	1.898	0.200	0.210	1.12 (0.97)
$(CH_3)_4AsCl$	0.480	0.003	1.085	0.142	0.118	0.22
$(CH_3)_3SeCl$	0.536	0.052	1.962	0.105	0.162	1.04
$(CH_3)_3TeCl$	0.339	0.021	1.980	0.073	0.153	0.45

These data except bond populations were supplied by the ASMO SCF calculations on the most energetically stable onium chlorides: the bond populations were calculated by the extended Hückel method.

a) R_{max} and those in parentheses stand for the rates in cumene and α-pinene oxidations respectively. Without an onium catalyst, $R_{max}\times 10^4$ was 0.17 or 0.34 mol/*l* sec in cumene or α-pinene oxidation respectively.



already demonstrated that the planar C_{3v} symmetry is the most plausible for the molecular geometry of the carbonium compound,[7] which is analogous with that of an oxonium compound. With respect to the bond length between the central atom and the counteranion, we can predict the ionic bond length on the baiss of the reaction system containing polar oxidation products, such as hydroperoxides and alcohols, although the present calculations on carbonium and oxonium chlorides do not provide the minimum values of their potential surfaces. Concerning the plausibility of the ionic bond length between the central atom and the counteranion, our previous detailed calculations on trimethylsulfonium chloride also supported this concept.[3–5] Therefore, the ionic bond length can be adopted for the other onium chlorides, though some

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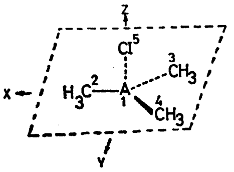
[7] D. W. A. Sharp and N. Sheppard, *J. Chem. Soc.*, **1957**, 674.

Table 3. Contributions of the neighboring atoms to the partial occupation of d_{xz} or d_{xy} orbital of onium central atom (A) in $(CH_3)_3ACl$

Central atom (A)	d-π Overlap				AO bond population			
	A–C[a)]		A–Cl		A–C[a)]		A–Cl	
	d_{xz}-p_z	d_{xy}-p_z	d_{xz}-p_x	d_{yz}-p_y	d_{xz}-p_z	d_{xy}-p_y	d_{xz}-p_x	d_{yz}-p_y
S	0.399	0.399	0.070	0.070	0.082	0.083	0.007	0.007
Se	0.368	0.368	0.078	0.078	0.010	0.007	0.006	0.006
Te	0.344	0.344	0.062	0.062	−0.019	−0.024	0.002	0.002

These data were supplied by EHMO calculations.

a) A–C bond corresponds to 1A-2C bond of $(CH_3)_3ACl$ illustrated in the following figure:



discrepancies yet remain in regard to the configuration of the silyl chloride. Moreover, the planar C_{3v} structure of trimethylsulfonium chloride[3–5)] may also support the analogous structures (planar C_{3v} ones) of onium chlorides containing Group VI elements as onium central atoms.

Secondly, the discussion will be developed with respect to the correlation between the electronic properties of onium compounds and their catalytic activities as oxidation catalysts. The order of the activity was found to be as follows: carbonium<ammonium< oxonium; (silyl)<phosphonium ≲ sulfonium; arsonium ≃ (telluronium) <selenonium. Among these-onium compounds, third-row onium compounds are most effective. The relatively low activity of the second-row onium compounds is probably due to the fact that their onium central atoms possess only the $2p_z$-orbital utilized for the interaction with the $(1\pi_g)_z$-orbital of O_2; the $2p_z$-orbital may not be so effective as d_{xz} and d_{yz} orbitals, in view of the orbital energy and the orbital overlap with the $(1\pi_g)_z$-orbital of O_2 (as to the mode of the interaction between the onium catalyst and O_2, see the simple model[8)] in Table 2). Another reason why the activity of the compound is low is that these onium compounds, especially the carbonium compound, are unstable and ionic. There exists, however, a parallelism between the catalytic activity of the second-row onium compounds and the atomic orbital (AO) population of the p_z-orbital of their central atoms (see Table 2). Some remarks should be here made. The catalytic activity is defined by the maximum reaction rate ($R_{\max}$ in Table 2), which is itself estimated from the quantity of O_2 absorbed (mol) in cumene (10 m*l*) or α-pinene (10 m*l*) oxidation at 85°C during the formation of a quantity of the hydroperoxides equal to that of the O_2 absorbed.

Concerning the electronic properties of third-, fourth-, and fifth-row onium compounds, they are characterized by their spatially far-reaching, partially-occupied d_{xz} (or d_{yz}) and d_{xy} orbitals utilized for the interaction with the $(1\pi_g)_z$ and the $(1\pi_g)_y$ of O_2 on the basis of a strong $d\sigma$-$p\sigma$ type overlap and a weak $d\pi$-$p\pi$ type overlap[4)] respectively. The remarkable activity of sulfonium and phosphonium compounds is the result of the low-lying, partially-occupied $3d_{xz}$ (or $3d_{yz}$) and $3d_{xy}$ orbitals. The silyl compound, however, exhibits a low activity because of the vacant $3p_z$-orbital. The order of the activity is also in good agreement with that of the AO population of the d_{xz} (or d_{yz}) or the d_{xy}, as may be seen from Table 2. In the cases of phosphonium and arsonium compounds, some steric hindrances by the substituents of the interaction between the onium catalyst and O_2 should be taken into consideration. The partial electron occupation of the *d*-orbitals is the result of the *d*-π interactions between the *d*-orbitals of the central atom and the pi-orbitals of the counteranion or the substituents. From this point of view, the contributions of neighboring atoms (C and Cl) to the partial electron occupation of the d_{xz} or the d_{xy} are confirmed by the *d*-π overlaps recorded in Table 3.

The relatively low activity of the fourth- or fifth-row onium compounds may be ascribed to the diffuse 4*d* or 5*d* orbitals, especially $4d_{xz}$ or $5d_{xz}$, of their central arsenium, selenium, or tellurium. This diffuseness of the *d*-orbitals depresses their orbital overlaps with the $(1\pi_g)_z$-orbital of O_2 and is reflected in the orbital contour map of the next higher MO to the lowest unoccupied MO (LU+1 MO) of $(CH_3)_3TeCl$, as may

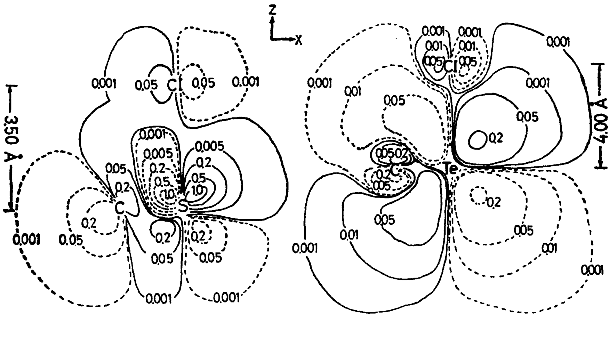


Fig. 1. Orbital contour maps of the LU+1 MOs of $(CH_3)_3SCl$ and $(CH_3)_3TeCl$. These MOs mainly come from the sulfur d_{xz}, carbon p_x and p_z, and chlorine p_x in the *x-z* cross section. (Solid and dotted curves indicate positive and negative MO-signs respectively.)

[8)] For detailed models of the interaction, see Ref. 4.

be seen when we compare the map with that of the LU+1 MO of $(CH_3)_3SCl$ (see Fig. 1).

Finally, it may be concluded that the partially-occupied 3*d*-orbitals are most effective for the catalytic activation of molecular oxygen, and that onium compounds possessing them on their central atoms exhibit a catalysis analogous with those of transition-metal catalysts.

The calculations were carried out on a FACOM 230.60 computer at the computation center of the University of Kyushu.