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A Theoretical Account of the Catalytic Behavior of Sulfonium Compounds in Oxidation Reactions

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In previous papers,[1,2] it has been emphasized that sulfonium compounds are the most effective catalysts in hydrocarbon oxidations among various onium compounds containing central atoms of C, N, O, P, S, As, Se, and Te, and that their catalytic activities are appreciably affected by the difference in counter anions and substituents attached to the central sulfur. This distinguished activity of the sulfonium compounds was well explained by their catalytic activations of molecular oxygen on the basis of the interaction between the partially-occupied sulfur *d*-orbitals and O_2: a strong $d\sigma$-$p\sigma$ type interaction between the sulfur d_{xz} (or d_{yz}) orbital and the $(1\pi_g)_z$-orbital of O_2, and a weak interaction between the sulfur d_{xy}-orbital and the $(1\pi_g)_y$-orbital of O_2.[3] The present study will try to clarify the catalytic behavior of the sulfonium compounds in oxidation reactions using an extended Hückel method[4] augmented by sulfur *d*-orbitals.

First, we will discuss the role of the counter anion and the substituents of the sulfonium compound in the catalytic activity. As Table 1 indicates, there is a parallelism between the catalytic activity (as estimated

TABLE 1. CORRELATION BETWEEN THE CATALYTIC ACTIVITY OF SULFONIUM COMPOUNDS AND THE AO POPULATIONS OF THE SULFUR *d*-ORBITALS UTILIZED FOR THE INTERACTION WITH $1\pi_g$-ORBITALS OF MOLECULAR OXYGEN

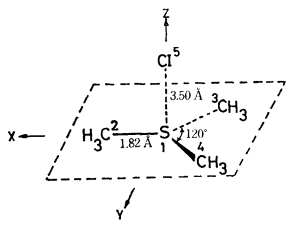
R_3SX[a]	S–X (Å)	M_{S-X}[b]	AO populations of S *d*-orbitals			$R_{max}\times 10^4$ [c] (mol/*l* sec)
			d_{xz}	d_{yz}	d_{xy}	
$(CH_3)_3SNO_3$	3.50	0.021	0.145	0.429	0.432	3.01
$(CH_3)_3SCl$	3.50	0.090	0.142	0.142	0.100	2.68
$CH_3)_3SBr$	3.80	0.071	0.142	0.142	0.100	2.60
$(CH_3)_3SI$	4.00	0.055	0.141	0.141	0.100	0.98
$(CH_3)_3SBF_4$	2.80	0.063	0.119	0.122	0.100	1.12
$(C_2H_5)_3SCl$	3.50	0.076	0.016	0.017	0.066	3.50
$(CH_3)_2C_6H_5SCl$	3.50	0.087	0.147	0.166	−0.011	2.52

a) ASMO SCF calculations on $(CH_3)_3SX$ demonstrated that the planar C_{3v} symmetrical sulfonium cation gave the most energetically stable $(CH_3)_3SX$[2].
b) Bond population of the S–X.
d) Maximum rates were estimated from O_2 absorbed (mol) which corresponds to the hydroperoxide formed (mol) in the cumene oxidation at 85°C (the amount of the sulfonium catalyst=3.0 mmol/*l*).

TABLE 2. CONTRIBUTIONS OF THE SULFUR *d*-ORBITALS TO THE ELECTRONIC PROPERTIES OF $(CH_3)_3S^+$ AND $(CH_3)_3SCl$

Compound	Atom population			Bond population		AO bond population					
						S–C[a]			S–Cl		
	S	C	Cl	S–C[a]	S–Cl	d_{xz}–p_z	d_{xy}–p_y	$d_{x^2-y^2}$–p_x	d_{xz}–p_x	d_{yz}–p_y	d_{z^2}–p_z
$(CH_3)_3S^+$ excluding S *d*-orbitals	6.379	3.748	—	0.576	—	—	—	—	—	—	—
$(CH_3)_3S^+$ including S *d*-orbitals	5.715	4.137	—	0.814	—	0.084	0.083	—	—	—	—
$(CH_3)_3SCl$ excluding S *d*-orbitals	5.260	4.255	7.995	0.699	−0.005	—	—	—	—	—	—
$(CH_3)_3SCl$ including S *d*-orbitals	5.773	4.145	7.919	0.815	0.092	0.092	0.083	0.004	0.007	0.007	0.054

a) S–C bond corresponds to 1S-2C bond of $(CH_3)_3SCl$ illustrated in the following figure:



1) K. Fukui, K. Ohkubo, and T. Yamabe, This Bulletin, **42**, 312 (1969).
2) K. Ohkubo, *Tetrahedron Lett.*, **1971**, 2571, 2897.
3) K. Ohkubo and T. Yamabe, This Bulletin, **44**, 1183 (1971).
4) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); *ibid.*, **40**, 2474, 2480, 2745 (1964); the Coulomb integrals of the sulfur *d*-orbital and the oxygen 2*p*-orbital were taken to be −7.00 eV and −13.61 eV respectively.

by the maximum reaction rate, R_{max}) and the AO populations of the d_{xz}, d_{yz}, or d_{xy} sulfur orbital, with some irregularities caused by the gap between the configurations of the sulfonium compounds in the present calculations and those in the reaction system, or by some steric hindrances to the interaction between sulfonium compounds and O_2. This partial occupation of the sulfur *d*-orbitals is a result of the d–π interactions with the counter anion and the substituents, as can be seen from the electronic property of $(CH_3)_3SCl$ in Table 2, in which the electronic property of $(CH_3)_3S^+$ has been recorded in order to suggest the contribution of the counter chlorine. The counter anion and the substituents thus contribute to the partial occupation of the sulfur *d*-orbitals of the sulfonium compounds.

Second, let us discuss the interaction between the sulfonium compounds and molecular oxygen. The most likely mode of the interaction of molecular oxygen is parallel to the ligand plane of the sulfonium and occurs in the range of the distance between the sulfonium catalyst and O_2, 2.5—3.0 Å.[2] The d_{xz} (or d_{yz}) sulfur orbital of the sulfonium catalyst contributes predominantly to the catalytic activation of O_2 by means of interaction with the $(1\pi_g)_z$-orbital of O_2, as is shown in Fig. 1.[5]

Third, it is of interest to investigate the process of the hydrogen abstraction of the $(CH_3)_3SCl$–O_2 system

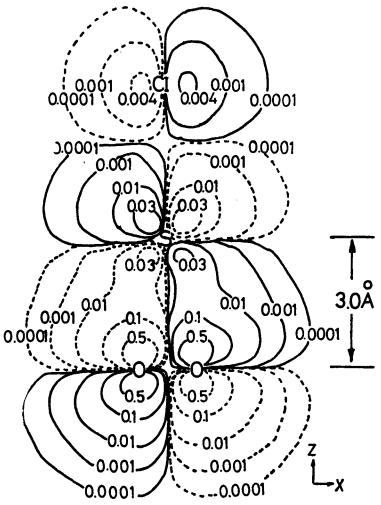


Fig. 1. The contour diagram for HO MO of the interacting system. This MO mainly comes from the interaction between $(1\pi_g)_z$ of O_2 and d_{zx} of $(CH_3)_3SCl$. (Solid and dotted curves indicate positive and negative MO-signs respectively.)

5) The contour diagram portrayed in Fig. 1 indicates the highest occupied molecular orbital (HO MO) of $(CH_3)_3SCl$–O_2. The $(1\pi_g)_z$-orbital of O_2 occupied most strongly the HO MO, in which, except for the d_{xz} orbital, the *p* and *d* orbitals of the central sulfur have negligible eigenvetors.

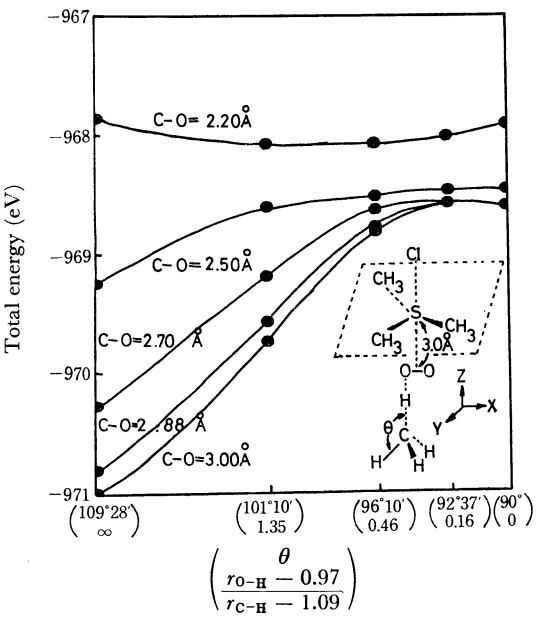


Fig. 2. Total energy changes in the process of hydrogen abstraction due to the stretching of the C–H and the variation of the bond angle of H–C–H (θ).

from hydrocarbons (CH_4 was used for the sake of simplicity of computation). The process was simulated by the stretching of the C–H in CH_4 (from C–H= 1.09 Å to H–O=0.97 Å), together with the change in the sp^3-hybrid structure of CH_4 to the sp^2-hybrid one, with the residual moiety retaining its equilibrium geometries (see Fig. 2). As Fig. 2 indicates, the transition state of the process seems to be situated near θ=92°37′, and the most plausible C–O distance falls in the range of 2.70—2.50 Å. The apparent activation energies calculated were 0.759 eV (2.50 Å), 1.652 eV (2.70 Å), 2.17 eV (2.88 Å), and 2.43 eV (3.00 Å), where the values in parentheses stand for the C–O distances. Some remarks should be here made: the activation energy in the other mode of interaction between the $(1\pi_g)_y$-orbital of O_2 and CH_4 was found to be higher than that in the interaction illustrated in Fig. 2 (for instance, 2.42 eV at C–O= 2.88 Å). In the hydrogen abstraction of O_2, O_2^-, and O_2^{2-} from CH_4 without sulfonium catalysts, the least activation energies were evaluated to be 2.04 eV (C–O=3.2 Å), 3.01 eV (C–O=3.5 Å), and 3.26 eV (C–O=3.8 Å) respectively; In other distances of C–O, the activation energies were higher. Sulfonium catalysts thus activate molecular oxygen and lower the activation energy required for the hydrogen abstraction from hydrocarbons.

The calculations were carried out on the FACOM 230.60 Computer at the Computation Center of Kyushu University.