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A THEORETICAL ACCOUNT FOR THE CATALYTIC ACTIVITY OF ONIUM COMPOUNDS IN THE LIQUID-PHASE OXIDATION

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Concerning the catalytic activity of onium compounds in the liquid-phase oxidation of hydrocarbons, the approximate order of the activity was found[1] as the combined results of cumene and α-pinene oxidations in the following: carbonium < ammonium<oxonium, silyl<phosphonium≤sulfonium, arsonium (≈telluronium)<selenonium, where the silyl was taken for comparison's sake. This experimental phenomena can be considered to relate immediately to the catalytic activation of molecular oxygen as suggested by the spectroscopic[2] and theoretical[3] investigations of the possible interaction between these oniums and O_2.
The interpretation of the catalytic activity of the oniums was intended with the extended Hückel method[4]. The total energies (E_{EH}) in Table 1 indicated that the stable structures of the trimethylonium chlorides take D_{3h} symmetrical cations and the preferable distance between the cation and the anion, while the tetramethyl-ammonium and -phosphonium have S_4 symmetrical cations.

The difference in the reasonably low activity of the oniums possessing the second law-central atoms would be due to that in the population on the p_z-orbital of the central atom. The distinguished activity of sulfonium- or phosphonium-compounds can be well explained by the contribution of the spacially far-reaching, partially occupied 3d-orbitals of the central sulfur or phosphor to the activation of O_2. Among the d-orbitals, d_{xz} or d_{yz} can be utilized most effectively for the interaction with $(1\pi_g)_z$-orbital of O_2 on the basis of the dp-σ overlapping[1]. In view of the electron donor-property of the oniums[1], the population of the vacant-like d-orbitals may thus play an important role in the catalytic activity. This partial occupancy of the d-orbitals is brought about by the d-π conjugation between the d-orbitals and pi-orbitals on the carbon of the substituents attached to the central atom as is reflected to the contour map of the wave function of trimethylsulfonium chloride at LU+1 level ~~in~~ Fig. 1.

On the other hand, the counter anion of the sulfonium or the phosphonium contributes to the partial occupancy of the d-orbitals. In the case of some sulfonium compounds, the order of the catalytic activity was found[1,5] to be as follow: the nitrate>the chloride≈the bromide>the iodide≈the tetrafluoroborate. This order is well reflected to the AO population on the sulfur d_{yz}-orbital (viz. 0.429, 0.142, 0.142, 0.100, and 0.090, respectively) resulting from the extended Hückel calculations of trimethylsulfonium derivatives.

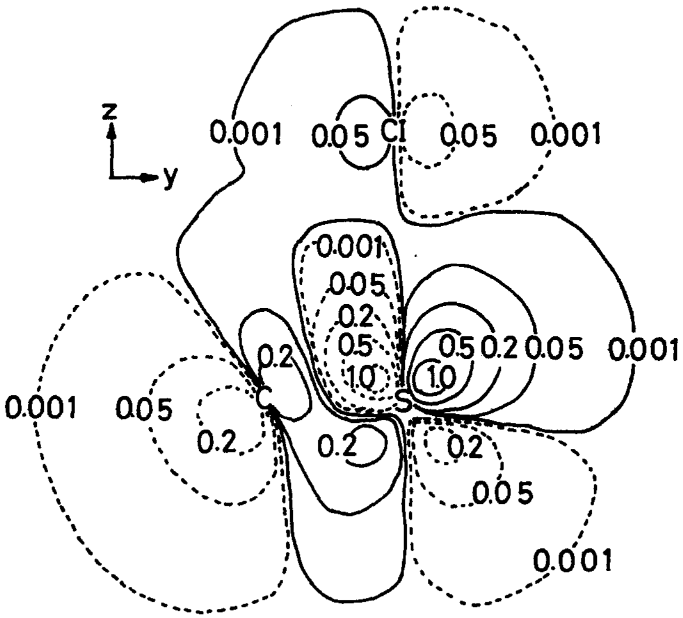

Fig. 1. The wave function contour of trimethylsulfonium chloride at LU+1 level.

Table 1. AO Populations of the Orbitals utilized for Interaction with $1\pi_g$-Orbitals of O_2.

Onium chloride R_3ACl or R_4ACl		A-Cl (Å)	AO Population						E_{EH} (eV)	$R_{max} \times 10^4$ a) (mol/l sec)
			p_z	d_{xz}	d_{yz}	d_{xy}	$d_{x^2-y^2}$	d_{z^2}		
$(CH_3)_3C$	D_{3h}	2.66	0.296						-548.34	0.26 (0.52)
$(CH_3)_4N$	S_4	3.30	1.267						-699.22	0.34 (0.74)
	D_{4h}	3.30	1.957						-688.78	
$(CH_3)_3O$	D_{3h}	3.90	1.980						-604.37	0.67 (0.82)
$(CH_3)_3Si$	D_{3h}	3.80	0.161						-541.25	(0.75)
$(CH_3)_3SiCl$	S_4	2.16	0.308						-541.12	
$(CH_3)_4P$	D_{4h}	3.70	0.453	0.137	0.137	0.056	-0.067	0.032	-679.98	(0.89)
	S_4	3.70	0.883	0.122	0.144	0.105	0.031	0.021	-683.88	
$(CH_3)_3S$	D_{3h}	3.50	1.981	0.142	0.142	0.092	0.092	0.068	-541.25	1.12 (0.97)
$(CH_3)_4As$	D_{3h}	3.80	0.427	-0.042	-0.042	-0.186	-0.517	-0.065	-680.89	0.22
	S_4	3.80	0.806	-0.125	-0.096	-0.119	-0.185	-0.202	-579.80	
$(CH_3)_3Se$	D_{3h}	3.70	1.989	0.020	0.020	-0.111	-0.111	-0.008	-576.16	1.04
$(CH_3)_3Te$	D_{3h}	4.00	1.991	-0.024	-0.024	-0.168	-0.174	-0.043	-575.08	0.45

a) R_{max} and those in parentheses were maximum rates estimated from the quantity of O_2 absorbed in cumene and α-pinene oxidations at 85°C, respectively, during the formation of equimolar quantity of the hydroperoxides to that of O_2 absorbed.

The relatively low activity of the arsonium and the telluronium would be ascribed to the vacant, diffused 4d- and 5d-orbitals, respectively, while the appreciable activity of the selenonium is caused by the partial electron-occupancy of selene $4d_{xz}$-(or $4d_{yz}$-)orbital.

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