Partially-occupied d-Orbitals Participating in the Activation of Molecular Oxygen

Katsutoshi Ohkubo
Department of Synthetic Chemistry, Faculty of Engineering, Kumamoto University, Kumamoto 860

(Received July 4, 1973)

UV spectroscopic and semiempirical SCFMO investigations have been performed on the partially-occupied (formally unoccupied) *d*-orbitals participating in the activation of the ground state, $^3\Sigma_g{}^-$-O_2, with special attention being given to the catalytic activities of onium compounds. The order of the red shifts of the $(p_z)^2 \rightarrow (p_z)(d)$ transition of the onium compounds in an oxygen atmosphere is in satisfactory accordance with those of the magnitude, of the partial occupancy of the *d*-orbitals and of the catalytic activities of the onium compounds in hydrocarbon oxidations. The d_{xz} (or d_{yz}) and $d_{x^2-y^2}$ orbitals are most favorably disposed for the interactions between the Group VI and V onium compounds and the $(1\pi_g)_z$-orbital of the $^3\Sigma_g{}^-$-O_2 respectively. The partial occupation of the formally unoccupied *d*-orbitals results from the *d*-π delocalization between the onium central atom and the neighboring atoms of substituents and the counter-anion.

The liquid-phase oxidation of hydrocarbons such as cumene, tetraline, xylenes, *etc.*, with onium compounds proceeds without any appreciable incubation period and accumulates only hydroperoxide as an oxidation product, at least for 1 hr after the start of reaction under the usual conditions.[1] Among onium compounds involving C, N, O, P, S, As, Se, and Te as their central atoms, the third-row onium (phosphonium and sulfonium) ones have been proved to be the most effective catalysts.[2,3] The distinguished activity of phosphonium compounds as well as of sulfonium compounds may be ascribed to their catalytic activation of the ground state, $^3\Sigma_g{}^-O_2$, during the initial stage of the reaction:[4,5]

$$\text{onium cat.} + O_2 \underset{2.898\times10^{9}\sqrt{T}e^{-21370/RT}}{\overset{9.389\times10^{9}\sqrt{T}e^{-19930/RT}}{\rightleftarrows}} \text{onium cat.}^{\delta+}\cdots O_2{}^{\delta-}$$

$$\text{onium cat.}^{\delta+}\cdots O_2{}^{\delta-} + RH \xrightarrow[\text{(rate determining)}]{1.447\times10^{10}\sqrt{T}e^{-22460/RT}} R\cdot + HO_2\cdot + \text{onium cat.}$$

$$R\cdot + O_2 \xrightarrow{8.538\times10^{9}\sqrt{T}e^{-6380/RT}} RO_2\cdot$$

$$RO_2\cdot + RH \xrightarrow{1.592\times10^{10}\sqrt{T}e^{-19300/RT}} ROOH + R\cdot$$

$$RO_2\cdot + RO_2\cdot \xrightarrow{1.582\times10^{10}\sqrt{T}e^{-10745/RT}} \text{inactive product}$$

$$\text{onium cat.} \xrightarrow{2.243\times10^{10}\sqrt{T}e^{-13104/RT}} \text{inactive form}$$

where the rate constants ($M^{-1}\,s^{-1}$ or s^{-1} unit) are those in the case of cumene oxidation catalyzed by triphenylsulfonium chloride.

With respect to the catalytic activation of the $^3\Sigma_g{}^-O_2$, other types of catalysts, such as copper phthalocyanine,[6,7] Cu-pc, and hemoglobin,[8-12] Globin-Fe, participate in the activation of the $^3\Sigma_g{}^-$ O_2:

$$\text{Cu-pc} + O_2 \longrightarrow \text{Cu-pc}^{\delta+}\cdots O_2{}^{\delta-}$$

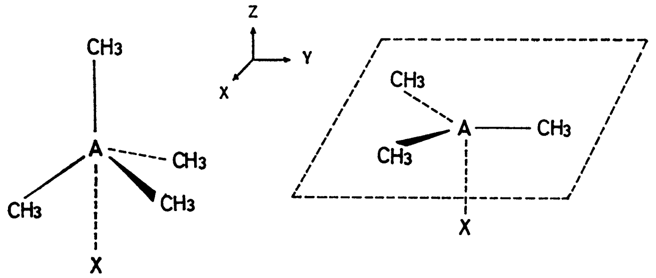
$$\text{Globin-Fe} + O_2 \rightleftarrows \text{Globin-Fe}^{+}\cdots O_2{}^{-}$$

No successful SCFMO calculation has hitherto been reported on the reaction systems mentioned above,[13] perhaps because there is difficulty in the accurate assessment of the relative locations of the states of O^+, O, and O^- on the energy scale and in the divergency of the SCF calculations.

The goal of the present study is to elucidate the role of partially-occupied (formally unoccupied) *d*-orbitals of onium compounds in the catalytic activation of the ground state, $^3\Sigma_g{}^-$ O_2, on the basis of UV spectroscopic measurements[14] and semi-empirical SCFMO calculations.[15]

Method of Calculation

The following three systems were investigated in this work: (a) trimethylsulfonium compounds, $(CH_3)_3SX$ (X=Cl, Br, I, BF_4, and ClO_4), (b) tetramethylphosphonium compounds, $(CH_3)_4PX$ (X=Cl, Br, I, BF_4, and ClO_4), and (c) trimethyl-selenonium and telluro-, nium chlorides, $(CH_3)_3SeCl$ and $(CH_3)_3TeCl$. The method of calculation is a semiempirical SCFMO, similar to the one described by Yonezawa *et al.*,[15] using the parametrization given in Ref. 16. The geometries used for calculations are illustrated in Fig. 1.



A=P C–P=1.87 Å C–H=1.10 Å CAX=CAC=109°28′
A=S, Se, or Te C–S=1.82 Å: C–Se=1.95 Å; C–Te=2.09 Å C–H=1.10 Å CAC=120°; CAX=90°

Fig. 1. Geometries of the onium compounds.

Results and Discussion

UV Spectroscopic Phenomena. Let us first discuss the UV spectroscopic phenomena concerned with the interaction between onium compounds and the $^3\Sigma_g{}^-$ O_2. Figure 2 presents the UV absorption spectra of $(C_6H_5)_4$-PCl, $(C_6H_5)_3SCl$, $(C_6H_5)_3SeCl$, and $(C_6H_5)_3TeCl$ in absolute ethyl alcohol at 25±1 °C in a nitrogen or oxygen atmosphere; the absorption curves of the said compounds indicate strong and reproducible peak, with absorption maxima, $\lambda_{max}(\log\varepsilon)$, of 204 (4.81)

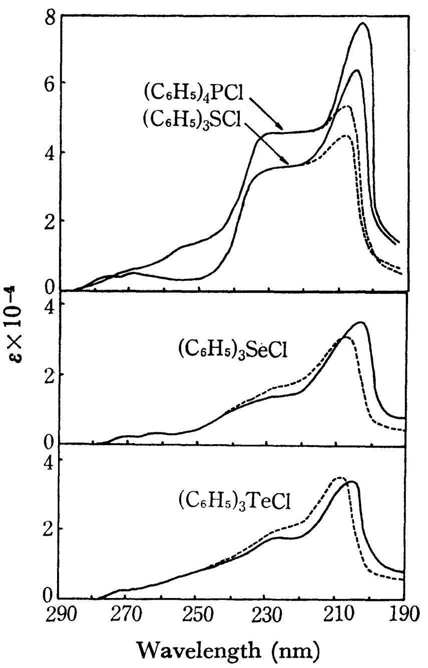


Fig. 2. UV absorption spectra of onium chlorides in C_2H_5OH at 25+1 °C. (Solid and dotted curves indicate the spectra in N_2 and O_2 atmospheres respectively.)

204 (4.88), 204 (4.56), and 205 nm (4.54) respectively in a N_2 atmosphere. These absorption peaks can be assigned to the electron excitation from the p-orbitals of the onium central atom to its d-orbitals, especially that from the p_z-orbital to the d_{z^2}-one, in view of the singlet excitation energies as evaluated by the SCFMO calculations. (Those for phosphonium chloride are shown in Fig. 3, while those for the others have already been discussed in Ref. 14.)

In an oxygen atmosphere, the above-mentioned peaks are shifted to longer wavelength regions ($\lambda_{\max}(\log \varepsilon)=$ 208 (4.65), 209 (4.73), 207.5 (4.50), and 208 nm (4.55) respectively). This is a result of the lowering of the low-lying, partially-occupied d-orbitals of the onium central atom, which results from the electron migration from the d-orbitals to the $1\pi_g$-orbitals of molecular oxygen through the plausible dp-σ type orbital overlappings to be shown later in this paper. That is, the more the electron densities of the d-orbitals decrease, the more their MO energy levels become lowered.

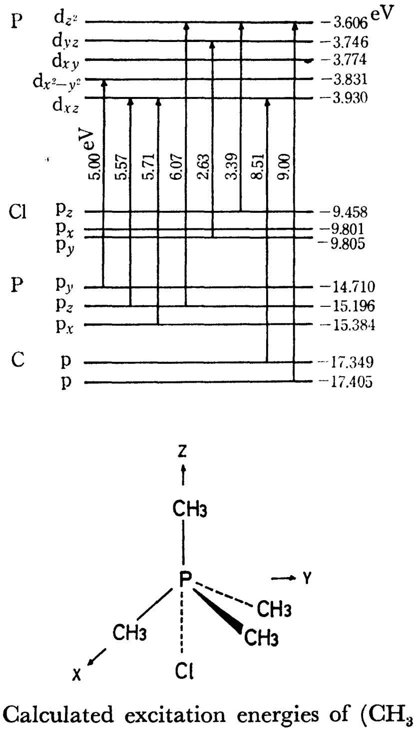


Fig. 3. Calculated excitation energies of $(CH_3)_4PCl$.

Interaction between the Partially-occupied d-Orbitals of Onium Compounds and the $1\pi_g$-Orbitals of the $^3\Sigma_g^-O_2$. Let us interpret briefly the molecular structures of onium compounds before discussing their interaction with the $^3\Sigma_g^-\ O_2$ in hydrocarbon oxidation. The energetically-stable phosphonium halides involve tetrahedral T_d onium cations, while the other oniums possess planar C_{3v} cations; the bond distance between the onium central atom and the counteranion has been proved to be a purely ionic one, particularly in polar solvents.[17] With regard to the structures of onium tetrafluoroborates and perchlorates (BF_4 and ClO_4), the planar C_{4v} counter-anions (B–F=1.40 Å; Cl–O=1.50 Å; ∠FBF=∠OClO=90°) have been, shown to give energetically-stable species.[18]

We should now consider the interaction between the partially-occupied d-orbitals and the $1\pi_g$-orbitals of the $^3\Sigma_g^-\ O_2$. In the Group VI onium (sulfonium, selenonium, and telluronium) compounds, a dp-σ type overlap between the d_{xy} (or d_{yz}) and the $(1\pi_g)_z$ is most predominant,[19] while in phosphonium compounds a dp-σ type orbital overlapping between the $d_{x^2-y^2}$ and the $1\pi_g$ is most probable, as is indicated in Fig. 4. It may be deduced, therefore, that the magnitude of the electron density on the d-orbitals (*viz.*, d_{xz} or d_{xy} and/or $d_{x^2-y^2}$) most favorably disposed for the interaction with the $1\pi_g$-orbitals of the $^3\Sigma_g^-\ O_2$ can be taken as a measure of the activation of the molecular oxygen.

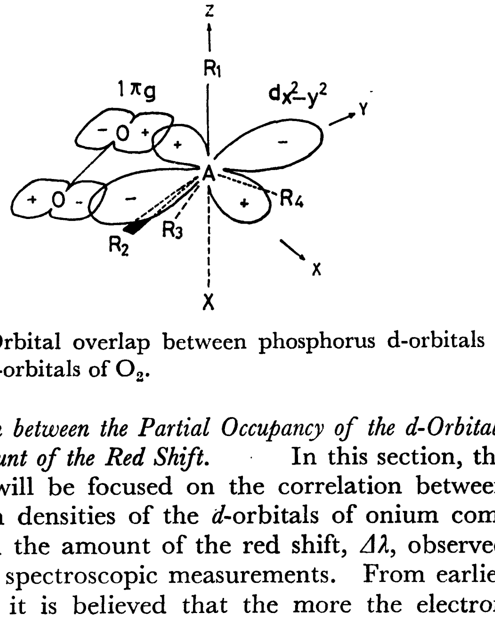


Fig. 4. Orbital overlap between phosphorus d-orbitals and $1\pi_g$-orbitals of O_2.

Correlation between the Partial Occupancy of the d-Orbitals and the Amount of the Red Shift. In this section, the discussion will be focused on the correlation between the electron densities of the d-orbitals of onium compounds and the amount of the red shift, $\Delta\lambda$, observed by the UV spectroscopic measurements. From earlier discussions, it is believed that the more the electron density of the d-orbitals of the onium central atom increases, the larger becomes the red shift of $\Delta\lambda$(eV), because the electron is expected to transfer from the onium compound to the $^3\Sigma_g^-$ O_2. Moreover, a parallelism may be expected between the $\Delta\lambda$ values and the catalytic activities of onium compounds, as defined by the maximum rate of oxygen absorption, R_{max}, in M/s units, during the initial stage of hydrocarbon (10 ml) oxidation with the onium compound (3.0 mM) at 85 °C. As can be seen from Table 1, the order of the electron densities of the d_{xz} (or d_{xy}) and/or $d_{x^2-y^2}$ orbitals accords with that of the $\Delta\lambda$ values and also with that of the R_{max} values.

TABLE 1. CORRELATION OF ELECTRON DENSITY OF PARTIALLY-OCCUPIED *d*-ORBITALS, AMOUNT OF RED SHIFT, $\Delta\lambda$, AND MAXIMUM OXIDATION RATE, R_{max}

Onium compound	Electron density			$\Delta\lambda$ (eV)	$R_{max}\times 10^4$ (Ms^{-1})	
	d_{xz}	d_{yz}	$d_{x^2-y^2}$		tetralin	cumene
$(CH_3)_4PCl$	0.216	0.191	0.189	0.12	7.44	
$(CH_3)_3SCl$	0.249		0.264	0.14	11.20	1.12
$(CH_3)_3SeCl$	01.05		0.162	0.104		1.04
$(CH^3)^3TeCl$	0.073		0.153	0.09		0.45
None					0.062	0.17

The correlation mentioned above is also realized in a series of sulfonium compounds, as is indicated in Table 2. Table 3 shows that the electron densities of the phosphorus $d_{x^2-y^2}$ orbital correlate well with the R_{max} values obtained from the tetralin oxidation under the conditions listes previously. The results shown in Tables 1, 2, and 3 are in harmony with the idea that the partially-occupied *d*-orbitals participate directly in the catalytic activation of the $^3\Sigma_g^-$ O_2. However, the *d*-orbital energy and the diffuseness of the *d*-orbital expansion should also be taken into consideration in discussing the interaction between the *d*-orbitals and O_2. In this respect, the relatively low activities of the fourth- or fifth-row onium compounds, such as selenonium and telluronium halides, may be ascribed to the diffuse 4*d* or 5*d* orbitals,[16,20] which may be unable to interact strongly with the $1\pi_g$-orbital of O_2.

TABLE 2. CORRELATION OF ELECTRON DENSITY OF SULFUR *d*-ORBITALS, AMOUNT OF RED SHIFT, $\Delta\lambda$, AND MAXIMUM OXIDATION RATE, R_{amx}

Sulfonium compound	Electron density $d_{xz}=d_{yz}$	$\Delta\lambda$(eV)	$R_{amx}\times 10^4$ (Ms^{-1}) tetralin
$(CH_3)_3SCl$	0.249	0.14	11.20
$(CH_3)_3SBr$	0.230	0.10	10.88
$(CH_3)_3SI$	0.212	0.05	3.80
$(CH_3)_3SBF_4$	0.171	0.03	0.56
$(CH_3)_3SClO_4$	0.148	0.02	0.30

TABLE 3. CORRELATION BETWEEN ELECTRON DENSITY OF PHOSPHORUS *d*-ORBITALS AND MAXIMUM OXIDATION RATE, R_{amx}

Phosphonium compound	Electron density					$R_{max}\times 10^4$ (Ms^{-1})
	d_{xy}	d_{yz}	d_{xy}	$d_{x^2-y^2}$	d_{z^2}	tetralin
$(CH_3)_4PCl$	0.216	0.191	0.180	0.189	0.450	7.44
$(CH_3)_4PBr$	0.216	0.194	0.179	0.185	0.342	7.00
$(CH_3)_4PI$	0.209	0.183	0.179	0.183	0.333	3.72
$(CH_3)_4PBF_4$	0.193	0.200	0.184	0.185	0.239	0.45
$(CH_3)_4PClO_4$	0.191	0.166	0.184	0.182	0.218	0.12

Here, it is necessary to discuss the chemical nature of the activated molecular oxygen. In an interacting system between the partially-occupied *d*-orbitals and the $1\pi_g$-orbitals, electron migrations from the former to the latter and from the $1\pi_u$-orbitals of the $^3\Sigma_g^-$ O_2 to the former may be expected. Such electron migrations increase the O–O bond distance of the oxygen molecule by means of the electron repulsion, and an odd-electron may be localized on each oxygen atom, thus increasing the radical nature of O_2. In this situation, the half-occupied, doubly-degenerate $1\pi_g$-orbitals come to be free from the degenerate state: for instance, a long-range interaction between $(CH_3)_3SCl$ and O_2 (S-Center of the O–O=3.0 Å) brings about the separation of the MO-energies of the $1\pi_g$-orbitals in an energy scale over 0.01 eV.[21] It may be worthy of emphasis here that the order of the catalytic activities: sulfonium$\gtrsim$phosphonium>selenonium>telluronium, is almost contrary to the lowering order of the energy levels of the d_{xz} (or d_{xy}) or the $d_{x^2-y^2}$: −4.8 eV for $(CH_3)_3TeCl$>−4.69 eV for $(CH_3)_3SeCl$>−4.38 eV for $(CH_3)_3SCl$>−3.83 eV for $(CH_3)_4PCl$. This may imply that the *d*-orbitals follow the initial charge to a higher π_g orbital (−0.15 eV[22,23]) rather than the $1\pi_g$ orbital (−12.075 eV) of the $^3\Sigma_g^-$ O_2.

Partial Occupation of the Formally Unoccupied d-Orbitals. Finally, mention should be made of the partial occupation of the formally unoccupied *d*-orbitals of onium compounds. The neighboring atoms of substituents and counter-anion participate directly in the partial occupation of the *d*-orbitals by the aid of the *d-π* (mainly, *dp-π*) delocalization between the central atom of the onium compound and the neighboring atoms. Table 4 shows the circumstances mentioned above in the case of phosphonium chloride; the *dd-π* delocalization between the phosphorus and the counter chlorine *d*-orbitals should also be taken into consideration.

TABLE 4. PARTIAL OCCUPATION OF PHOSPHORUS *d*-ORBITALS OF $(CH_4)_4PCl$

Species	Basis set		Atom population		Electron density	
	P	Cl	P	Cl	$d_{x^2-y^2}$	d_{z^2}
$(CH_3)P_4^+$	*s,p*		5.089			
$(CH_3)_4P^+$	*s,p,d*		5.430		0.1706	0.1716
$(CH_3)_4PCl$	*s,p*	*s,p*	5.061	7.982		
$(CH_3)_4PCl$	*s,p,d*	*s,p*	5.629	7.538	0.1889	0.1803
$(CH_3)_4PCl$	*s,p,d*	*s,p,d*	5.647	7.520	0.1895	0.1805

Therefore, the more electron-releasing groups of substituents or counteranions are attached to the central atoms, the higher becomes the catalytic activity of the onium compounds. This is in harmony with the experimental phenomena observed in the liquid-phase oxidation of hydrocarbons with various onium compounds.[2,3]

References

1) K. Ohkubo, T. Yamabe, and K. Fukui, This Bulletin, **42**, 2220 (1969).

2) K. Fukui, K. Ohkubo, and T. Yamabe, *ibid.*, **42**, 312 (1969).

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

4) K. Ohkubo, T. Yamabe, and K. Fukui, This Bulletin, **42**, 1800 (1969).

5) K. Ohkubo and T. Hashimoto, *ibid.*, **45**, 3350 (1972).

6) H. Kropf, *Ann.*, **637**, 73 (1960).

7) H. Kropf and Hd. Hoffmann, *Tetrahedron Lett.*, **1967**, 659.

8) L. Pauling and C. D. Coryell, *Proc. Natl. Acad. Sci. U. S.*, **22**, 210 (1936).

9) L. Pauling, *Nature*, **203**, 182 (1964).

10) J. S. Griffith, *Proc. Roy. Soc., Ser. A*, **235**, 23 (1956).

11) J. J. Weiss, *Nature*, **202**, 83 (1964); *ibid.*, **203**, 183 (1964).

12) R. D. Harcurt, *Int. J. Quantum Chem.*, **5**, 479 (1971).

13) The extended Hückel MO treatment of the interacting system between sulfonium compounds and the $^3\Sigma_g^-O_2$ can be seen in the following paper: K. Ohkubo and H. Kanaeda, This Bulletin, **45**, 11 (1972).

14) With respect to the technique of the UV spectroscopic measurements, see K. Ohkubo and T. Yamabe, *J. Org. Chem.*, **36**, 3149 (1971).

15) For instance, see H. Kato, H. Konishi, and T. Yonezawa, This Bulletin, **40**, 1017 (1967).

16) K. Ohkubo and H. Kanaeda, *J. Chem. Soc., Faraday Trans. II*, **68**, 1164 (1972).

17) K. Ohkubo and H. Kanaeda, This Bulletin, **45**, 1571 (1972).

18) K. Ohkubo and H. Sakamoto, *Chem. Lett.*, **1973**, 209.

19) K. Ohkubo and T. Yamabe, This Bulletin, **44**, 1183 (1971).

20) K. Ohkubo, *Tetrahedron Lett.*, **1971**, 2571.

21) K. Ohkubo, *ibid.*, **1971**, 2897.

22) D. S. Burch, S. J. Smith, and L. M. Branscomb, *Phys. Rev.*, **112**, 171 (1958).

23) R. S. Mulliken, *ibid.*, **115**, 1225 (1959).