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ROLE OF THE PARTIALLY-OCCUPIED d-ORBITALS OF PHOSPHONIUM COMPOUNDS IN THE CATALYTIC ACTIVATION OF MOLECULAR OXYGEN IN LIQUID-PHASE OXIDATION

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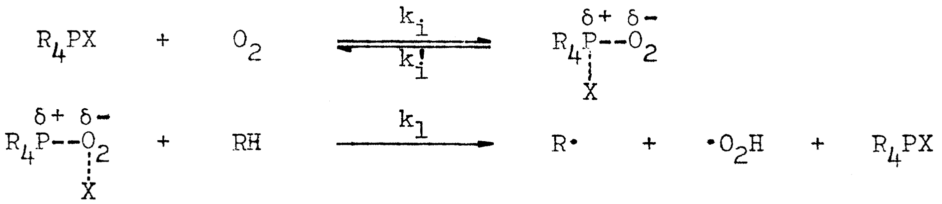
The catalytic activation of the ground state $^3\Sigma_g^-\ O_2$ by phosphonium compounds in the liquid-phase oxidation of hydrocarbons was demonstrated on the basis of ultraviolet spectroscopic measurements and ASMO-SCF calculations. The said compounds, namely, activate the $^3\Sigma_g^-\ O_2$ mainly by the aid of the electron-transfer from the partially-occupied phosphorus $d_{x^2-y^2}$-orbital of the formers to the $1\pi_g$-orbitals of the latter through the favorable d-π orbital-overlaps.

In the previous paper,$^{1)}$ phosphonium compounds (R_4PX) have been pronounced as an effective catalyst for the liquid-phase oxidation of hydrocarbons (RH) such as cumene, tetralin, xylenes, etc. The distinguished activity of said compounds as well as sulfonium ones may be ascribed to their catalytic activation of the ground-state molecular oxygen during the initial stage of reaction:



$$R_4PX + O_2 \underset{k_i'}{\overset{k_i}{\rightleftharpoons}} \underset{X}{\overset{\delta+\ \delta-}{R_4P\text{--}O_2}}$$

$$\underset{X}{\overset{\delta+\ \delta-}{R_4P\text{--}O_2}} + RH \xrightarrow{k_1} R\cdot + \cdot O_2H + R_4PX$$

where the rate constants of k_i, k_i', and k_1 are $2.23 \times 10^{-2}\ mol^{-1}l\,sec^{-1}$, $0.82 \times 10^{-3}\ sec^{-1}$, and $0.794 \times 10^{-3}\ mol^{-1}l\,sec^{-1}$ respectively, in the case of triphenylsulfonium chloride.$^{2)}$ The presumption made above is consistent with the following experimental observations: The oxidation reaction proceeds without any appreciable incubation period with an accumulation of hydroperoxide as the only oxidation product for at least 1 hr after the start of reaction under the usual conditions, and the interaction between the sulfonium compounds and O_2 is confirmed by the UV spectroscopic investigation.[3)]

The present study was undertaken to elucidate the role of the partially-occupied d-orbitals of phosphonium compounds in the catalytic activation of the ground state $^3\Sigma_g^-$ O_2 on the basis of UV spectroscopic measurements and ASMO-SCF calculations.

As to the molecular structure of phosphonium compounds, the ASMO-SCF calculations on R_4PX (X=halogen)[4,5)] in their two distinctive configurations (the planar C_{4v} and the tetrahedral T_d phosphonium cations) have supported the conclusion that the latter form was energetically more stable and suggested that the purely ionic distance of P-X bond is existed as the suitable location of counteranion, particularly in polar solvents.

With regard to the structures of R_4PBF_4 and R_4PClO_4, the planar C_{4v} counter-anions (B-F=1.40 Å; Cl-O=1.50 Å; $\angle FBF=\angle OClO=90^\circ$) were shown to give energetically stable species.[6)]

In discussing the interaction between phosphonium compounds and molecular oxygen, the UV absorption spectra of $(C_6H_5)_4PBr$ (one of markedly effective catalysts) in C_2H_5OH under nitrogen or oxygen atmosphere are presented in Fig. 1, together with that of $(C_6H_5)_3SCl$ for the sake of comparison. The absorption curve for $(C_6H_5)_4PBr$ indicates a strong and reproducible peak with an absorption maximum (λ_{max}) at 204 nm (log ε =4.81) under nitrogen atmosphere. This absorption peak can be assigned to the electron-transfer from p-orbitals of the central phosphorus atom to its d-orbitals, especially, that from p_z-orbital to d_{z^2}-one (see Fig. 2); While, under oxygen atmosphere, the above-mentioned peak is shifted to the longer wave-length region (λ_{max}=208 nm and log ε=4.65). This is due to the lowering the partially-occupied phosphorus d-orbitals, which is resulted from

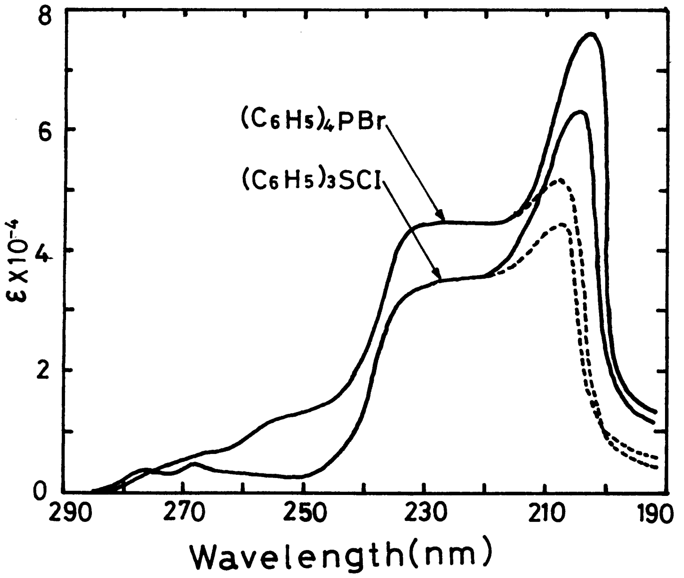


Fig. 1. UV spectra of $(C_6H_5)_4PBr$ and $(C_6H_5)_3SCl$ in C_2H_5OH at 25±1°C. Solid and dotted curves indicate those in N_2 and O_2 atmospheres respectively.

Table 1. Correlation between $\Delta\lambda$ and R_{max} Values.

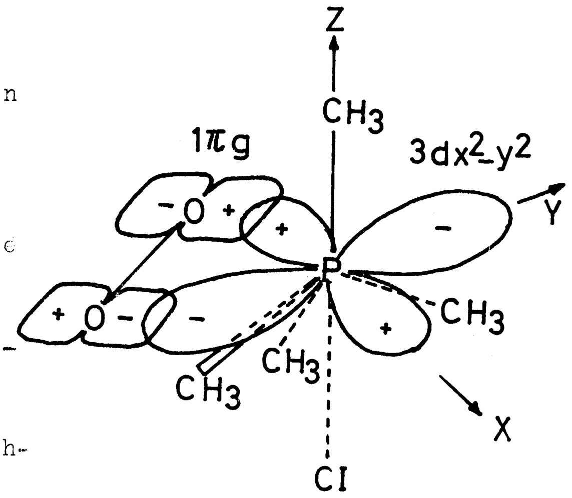
Onium compound	Temperature (^{o}C)	$\Delta\lambda$ (eV)	$R_{max} \times 10^4$ (mol/l.sec)[a] Tetralin	Cumene	α-Pinene
$(C_6H_5)_4PBr$	25±1	0.12	7.44	0.89	
$(C_6H_5)_3SCl$	25±1	0.14	11.2	0.97	1.12
$(C_6H_5)_3SeCl$	25±1	0.104			1.04
$(C_6H_5)_3TeCl$	25±1	0.09			0.45
none			0.062	0.17	0.34

Table 2. Correlation between Electronic Properties of Phosphonium and Some Other Onium Compounds and Their Catalytic Activities.

Onium compound R_3AX or R_4AX	A-X (Å)	Formal charge of central atom	Dipole moment (debye)	Electron density of phosphorus d-orbitals d_{xz}	d_{yz}	d_{xy}	$d_{x^2-y^2}$	d_{z^2}	$R_{max} \times 10^4$ [a] (mol/l.sec)
$(CH_3)_4PCl$	3.70	-0.629	8.960	0.216	0.191	0.180	0.189	0.450	7.44
$(CH_3)_4PBr$	3.85	-0.564	11.378	0.219	0.194	0.179	0.185	0.342	7.00
$(CH_3)_4PI$	4.05	-0.549	12.787	0.209	0.183	0.179	0.183	0.333	3.72
$(CH_3)_4PClO_4$	3.20	-0.507	13.175	0.191	0.166	0.184	0.182	0.218	0.12
$(CH_3)_4PBF_4$	2.85	-0.526	9.195	0.193	0.200	0.194	0.185	0.239	0.45
$(CH_3)_3SCl$	3.50	-0.810	7.088	0.200	0.200	0.210	0.210	0.446	11.2
$(CH_3)_4NBr$	3.45	-0.342	15.522						0.30
$(CH_3)_2H_2NBr$	3.45	-0.285	16.422						0.30

[a] R_{max} values were obtained from the oxygen absorption in the liquid-phase oxidation of tetraline (10 ml) or some other hydrocarbons (10 ml) at 80°C with the onium catalyst (3.0 mmol/l). In Table 2, they were obtained in the tetralin oxidation.

the electron-transfer from the phosphorus d-orbitals (especially, $d_{x^2-y^2}$) to the $1\pi_g$-orbitals of O_2 through the following plausible orbital overlapping: Namely, the more the electron density of the d-orbitals decreases, the more their energy levels become lowered. The smaller energy requirement for the transition is probably because of the lessening of electron repulsion on the d-orbitals by the partially-occupied electron as well as of the screening of the nuclear charge by them. On the other hand, the solvent such as C_2H_5OH may bring about the elevation of the d-orbitals through its solvation effect.[7]



The electrons transferred from the phosphonium compound to O_2 may bring about the stretching of O-O bond becuase of the electron repulsion on O_2 and increase the reactivity of O_2 in the hydrogen abstraction.[8] It may be deduced, therefore, that the amount of red shift ($\Delta\lambda$) mentioned above is in parallel with the catalytic activity of onium catalysts. Here, the catalytic activity is defined tentatively by the maximum rate of oxygen absorption, R_{max}, during the initial stage of hydrocarbon oxidation.

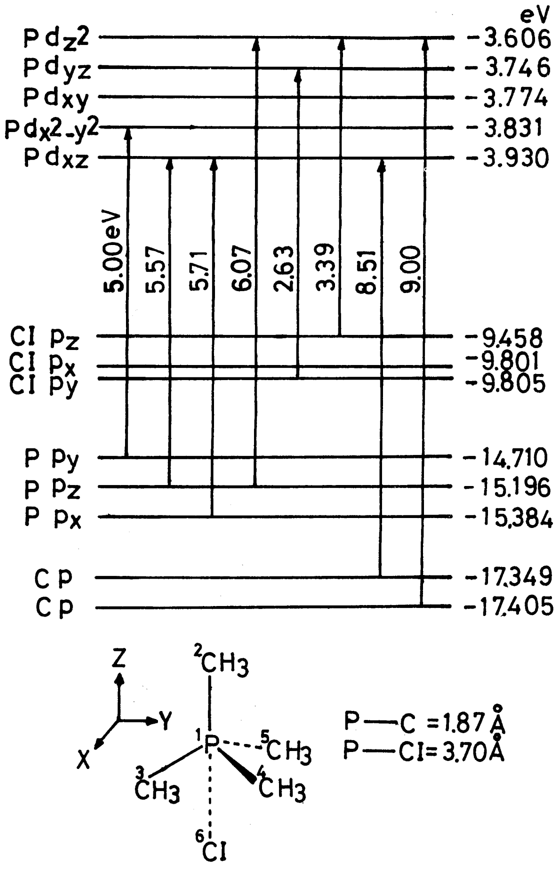


Fig. 2. Transition energies of $(CH_3)_4PCl$ in its ionic structure.

The correlation between $\Delta\lambda$ (eV) and R_{max} (mol/lsec) of phosphonium and some other onium compounds is indicated in Table 1. As can be seen from Table 1, the order of $\Delta\lambda$ values is in satisfactory accordance with that of R_{max} ones.

Remarks should be here made of the correlation between the catalytic activity of several phosphonium compounds and the electronic properties of d-orbitals on the central phosphorus atom.

Table 3. Electronic Properties of $(CH_3)_4\overset{+}{P}$ and $(CH_3)_4PCl$ with or without Phosphorus or Chlorine d-Orbitals.

Species	Atom population			Bond population		Electron density on P	
	P	C$^{a)}$	Cl	P-C$^{a)}$	P-Cl	$d_{x^2-y^2}$	d_{xy}
$(CH_3)_4\overset{+}{P}$ excluding P d-orbitals (I)	5.089	3.740					
$(CH_3)_4\overset{+}{P}$ including P d-orbitals (II)	5.430	3.887				0.1706	0.1716
$(CH_3)_4PCl$ excluding P and Cl d-orbitals (III)	5.061	3.771	7.982	0.00015	0.0		
$(CH_3)_4PCl$ including P d-orbitals (IV)	5.629	3.895	7.538	0.03384	0.00025	0.1889	0.1803
$(CH_3)_4PCl$ including P and Cl d-orbitals (V)	5.647	3.895	7.520	0.03306	0.00539	0.1895	0.1805

Species	AO bond population										
	P-C$^{a)}$			P-Cl							
	$d_{xz}-p_x$	$d_{yz}-p_y$	$d_{z^2}-p_z$	$d_{xz}-p_x$	$d_{yz}-p_y$	$d_{z^2}-p_z$	$d_{xz}-d_{xz}$	$d_{yz}-d_{yz}$	$d_{xy}-d_{xy}$	$d_{x^2-y^2}-d_{x^2-y^2}$	$d_{z^2}-d_{z^2}$
(IV)	0.02275	0.02077	-0.00045	0.000005	0.000004	0.00007					
(V)	0.02242	0.02046	-0.00045	0.000005	0.000004	0.00007	0.00112	0.00253	0.00053	-0.00019	0.00108

a) These carbon atoms are 2C atoms indicated in Fig. 2.

(Geometries used for the calculations are same ones in Fig. 2).

From the discussions made above, it is believed that the more the electron density of phosphorus d-orbitals (especially, $d_{x^2-y^2}$) increases, the higher the catalytic activity of phosphonium compounds become, since the electron-transfer from the phosphonium to molecular oxygen will increase with respect to the phosphorus d-orbitals with larger electron density. In Table 2 are listed the electron densities of the d-orbitals of several phosphonium compounds and R_{max} values obtained in tetralin oxidation. From the Table 2, the order of R_{max} values is well reflected in the electron densities of phosphorus $d_{x^2-y^2}$ orbital and sulfur d_{xz} (or d_{yz}) orbital.[5,7]

It may be seen from Table 3 that the neighboring atoms attached to the central phosphorus atom play an important role in the partial occupation of phosphorus d-orbitals, namely, the d-π (mainly, dp-π) delocalization between the phosphorus and the neighboring atoms contributes directly to the partial occupation of the d-orbitals. Here, the dd-π delocalization between the phosphorus and counter chlorine d-orbitals should be taken into consideration.

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4) With regard to the details of calculation method and results, see K. Ohkubo and H. Kanaeda, Trans. Faraday Soc., 68, 1164 (1972).

5) K. Ohkubo and H. Kanaeda, Bull. Chem. Soc. Japan, 45, 1571 (1972).

6) For instance, the total energy of $(CH_3)_4PX$ (X=planar C_{4v} BF_4 or ClO_4) is -1892.76eV or -1527.95eV respectively, while that of $(CH_3)_4PX$ (X=tetrahedral T_d BF_4 or ClO_4) is -1881.25eV or -1522.09eV respectively.

7) The transition energy increases with the increase in the polality, hence in the stabilization energy, of the solvents (see Ref. 3).

8) K. Ohkubo and H. Kanaeda, Bull. Chem. Soc. Japan, 45, 1550 (1972).

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