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Semi-empirical SCF-MO Studies of Pd(II)- and Hg(II)-Ethylene Complexes, the Oxymercuration and the Wacker Reaction

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Using the modified CNDO MO method, the electronic structures of Pd(II)- and Hg(II)-ethylene complexes have been studied successfully. Our MO calculations have shown that the nucleophilic attack of OH^- on ethylene was accelerated by Pd(II) and Hg(II), and that the acceleration by Hg(II) was larger than that by Pd(II), these results agree well with those of the experiments. The *cis*-attack of OH^- in the oxymercuration has also been discussed by the use of the results obtained by the MO calculations. The mechanism of the *cis*-type four-center addition of OH^- to ethylene in the Wacker reaction, which was supposed by Henry and Jira *et al.* in spite of any direct evidence, has been supported by the MO calculations. Our calculations have been able to explain the Markovnikoff rule in the Wacker reaction and in the oxymercuration of propylene.

A number of reactions of nucleophilic attack on olefins coordinated to a metal ion are well known.[1—3] Complex formation reduces the electron density between the carbon atoms of double bond, rendering the double bond more susceptible to nucleophilic attack. This must be the first requisite for the catalytic ability of transition metal ions in nucleophilic reactions. It is, therefore, interesting from the viewpoint of catalytic chemistry to investigate the electronic structures of olefins coordinated to transition-metal ions. There have, though, been few MO studies[4,5] of such transition-metal olefin complexes supposed to be intermediates in catalytic reactions.

The Wacker reaction[1—3] and the oxymercuration[6,7] are known as nucleophilic reactions onto a coordinated olefin; in them Pd(II)- and Hg(II)-olefin complexes are considered to be reaction intermediates. We carried out MO calculations of Pd(II)- and Hg(II)-olefin complexes in order to investigate the electronic structures of the coordinated olefins and discussed the catalytic activities of Pd(II) and Hg(II). Also, using the MO method, we studied whether the *cis*-addition occurs in the oxymercuration, or whether the *trans*-addition does, and whether or not the *cis*-addition of OH^- in the Wacker reaction is a reasonable mechanism; these problems have never been discussed theoretically. Since some work[8,9] using the Iterative Extended Hückel MO method has been done to investigate the catalytic reactions, it is also our object to examine the possibility of applying the more accurate semi-empirical SCF-MO method to studies in the field of catalytic chemistry.

Calculation and Models

Calculation. All the valence orbitals, including the 5d-atomic orbitals of the Hg atom, were considered explicitly. The modified CNDO-type approximation was used; the Hartree-Fock matrix elements have been given in our previous papers.[10] The resonance integral, $\boldsymbol{H}_{rs}$ $(r \neq s)$, was calculated according to the Wolfsberg-Hermholz approximation:[11]

$$\boldsymbol{H}_{rs} = -kS_{rs}(\boldsymbol{I}_r+\boldsymbol{I}_s) \qquad (1)^{12)}$$

In order to determine the value of k, the MO's of ethylene, propylene, methane, carbon monoxide, and formaldehyde were calculated using various values of k. That is, as to the MO energies of ethylene and the ionization potentials of these compounds, the best-fitting value of k was 0.40.[13] Hereafter, the value of k will be taken as 0.40 for all s and p orbitals. For the AO pair including the d-orbital, the value of k was determined to be equal to 0.50, thus the calculated first and second d-d transitions of $PdCl_4^{-2}$ coincide with the experimental results, as is shown in Table 1.

TABLE 1. THE FIRST AND SECOND d-d TRANSITION ENERGIES OF $PdCl_4^{-2}$

k	0.55	0.50	Obsd	
$^1A_{2g}$	2.62 (eV)	2.54 (eV)	2.62 (eV)[a]	2.48 (eV)[b]
^1E_g	3.40	3.44		2.80

a) Ref. 15. b) Ref. 16.

The values of the ionization potentials, $\boldsymbol{I}_r$, and the one-center Coulomb repulsion integrals, γ_{rr}, of ligand atoms were taken from Jaffé *et al.*,[16] while those values of the Pd atom were taken from Di Sipio *et al.*[17] Since those values of the Hg atom were not given in the paper of Di Sipio *et al.*, the values of $\boldsymbol{I}_r$ were taken from Bach's paper[18] and those of γ_{rr} were estimated as follows;

$$\gamma_{rr}(6)_{\text{semi-emp}}/\gamma_{rr}(5)_{\text{semi-emp}} = \gamma_{rr}(6)_{\text{nonemp}}/\gamma_{rr}(5)_{\text{nonemp}} \qquad (2)$$

where $\gamma_{rr}(5)$ and $\gamma_{rr}(6)$ represent the one-center Coulomb repulsion integrals of a fifth-row element and a sixth-row element, which belong to the same group in the periodic table, respectively. The subscripts "semi-emp" and "nonemp" indicate the semi-empirical value and the nonempirical value of γ_{rr} respectively. $\gamma_{rr}(N)_{\text{nonemp}}$ $(N=5$ or $6)$ was calculated using Clementi's AO,[19] and $\gamma_{rr}(5)_{\text{semi-emp}}$ was taken from Di Sipio's paper.[17] Then the γ_{rr} (6) values used in this work were obtained from the values of $\gamma_{rr}(6)_{\text{semi-emp}}$ by applying the least-squares method and by imposing the restrictive condition[17] that the values of $\gamma_{rr}(6)$ varied linearly with the atomic number. In order to calculate the overlap integrals, a single Slater-type orbital[19,20] was used for all the s- and p-orbitals; the

TABLE 2. ORBITAL EXPONENT (ζ_r), VALENCE STATE IONIZATION POTENTIAL (I_r), AND ONE-CENTER COULOMB REPULSION INTEGRAL (γ_{rr}) OF Pd AND Hg ATOMS

Atom	AO	ζ_r[a]	C[b]	I_r	γ_{rr}
Pd	4d	5.983 2.613	0.5264 0.6373	8.17 (eV)[c]	13.87 (eV)[c]
	5s	2.190		7.07	7.46
	5p	2.190		3.30	6.22
Hg	5d	6.436 3.032	0.6667 0.5401	15.66 (eV)[d]	13.53 (eV)[e]
	6s	2.649		10.44	7.40
	6p	2.649		5.00	6.31

a) The double-ζ form AO's are used only for d orbitals (Ref. 21). b) Because we neglect the contribution of the 3d orbital in the case of the Pd atom and the contributions of the 3d and 4d orbitals in the case of the Hg atom, the 4d orbital of the Pd atom and the 5d orbital of the Hg atom are renormalized in this work. c) Ref. 17. d) Ref. 18. e) The estimated values.

double-ζ-form orbital[21] was used only for the d-orbitals of metal atoms. The values of the AO exponents, ζ_r, I_r and γ_{rr} of the Pd and Hg atoms are listed in Table 2.

We discussed the bond strength in terms of $\boldsymbol{E}_{AB}$,[22-24] the contribution of the interaction between A and B atoms to the total energy; it is written, using the approximations used in this work, as follows;

$$\boldsymbol{E}_{AB} = \boldsymbol{E}_{AB}^{(1)} + \boldsymbol{E}_{AB}^{(2)} + \boldsymbol{E}_{AB}^{(3)} \qquad (3)^{12)}$$

$$\boldsymbol{E}_{AB}^{(1)} = 2\sum_r^A \sum_s^B \boldsymbol{P}_{rs}\boldsymbol{H}_{rs} \qquad (4)^{12)}$$

$$\boldsymbol{E}_{AB}^{(2)} = -0.5\sum_r^A \sum_s^B \boldsymbol{P}_{rs}^2(rr|ss) \qquad (5)^{12)}$$

$$\boldsymbol{E}_{AB}^{(3)} = \sum_r^A \sum_s^B (\boldsymbol{N}_r-\boldsymbol{P}_{rr})(\boldsymbol{N}_s-\boldsymbol{P}_{ss})(rr|ss) \qquad (6)^{12)}$$

where $\sum^A$ represents the summation on the A atom.

Geometries of Pd(II)- and Hg(II)-Olefin Complexes. Because of the lack of knowledge of the accurate configurations of these compounds, the configurations of the olefin moieties in these complexes were assumed to be the same as those of the corresponding free olefins.[25] The distances between the metal atom and the center of the double bond were fixed as 2.31 Å for Pd(II) Complexes[25] and as 2.34 Å for the Hg(II) complexes.[4] The metal-olefin coordination bond was assumed to intercept the double bond perpendicularly at its center. The coordinate systems for these complexes are given in Fig. 1.

Models for the Oxymercuration and the Wacker Reaction. In the oxymercuration, both *cis*- and *trans*-addition products were formed from the strained olefins, such as norbornene and bicyclo-[2,2,2]-oct-2-ene,[7,26-29] although only a *trans*-addition product was formed from nonstrained olefins.[6] Therefore, it is meaningful to shed some light on the course of the addition using an MO method. Since mercurinium ions have been postulated as intermediates in oxymercurations of olefins,[6,30] we assumed both *cis*- and *trans*-oxymercurials were derived from a common mercurinium ion, and calculated the MO's of the models for *cis*- and *trans*-addition (cf. Fig. 2). In order to ascertain the effects of reactants and ligands, we calculated the MO's of reaction systems, such as $Hg(C_2H_4)^{+2}\leftarrow OH^-$, $HgCl(C_2H_4)^+\leftarrow OH^-$, $HgCl(C_3H_6)^+\leftarrow OH^-$, HgCl(*cis*-2-$C_4H_8)^+\leftarrow OH^-$, and HgCl(*trans*-2-$C_4H_8)^+\leftarrow OH^-$, in which OH^- was assumed to approach olefin in the *trans* position of Hg(II) (see Fig. 3.), since the *trans*-oxymercurials were formed in general.

In the case of the Wacker reaction, an oxypalladate intermediate has not been observed. However, its existence has been postulated on the basis of kinetic studies[31-35] and the step of its formation from Pd(II)-olefin complex has been considered to be the rate-

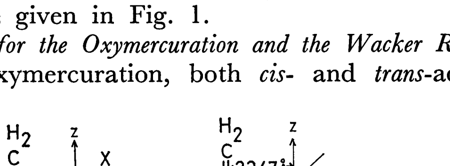


Fig. 1. The coordinate systems of Pd(II)- and Hg(II)-ethylene complexes.
X=F, Cl, Br
Pd-F: 1.88 Å[a], Pd-Cl: 2.23 Å[b], Pd-Br: 2.35 Å[a]
Hg-F: 1.84 Å[b], Hg-Cl: 2.29 Å[b], Hg-Br: 2.41 Å[b]
a) The estimated value. b) Ref. 25.

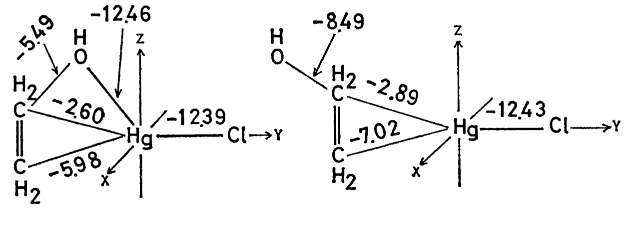


Fig. 2. The values of $\boldsymbol{E}_{AB}$[a] in the *cis*- and *trans*-addition of oxymercuration.
a) eV unit, b) The relative position of OH^- to ethylene is the same as that of *cis*-addition system. C-O=1.72 Å and Hg-O (in *cis*-configuration)=2.03 Å. c) $\boldsymbol{E}_{total}=-2164.3$ eV. d) $\boldsymbol{E}_{total}=-2159.8$ eV.

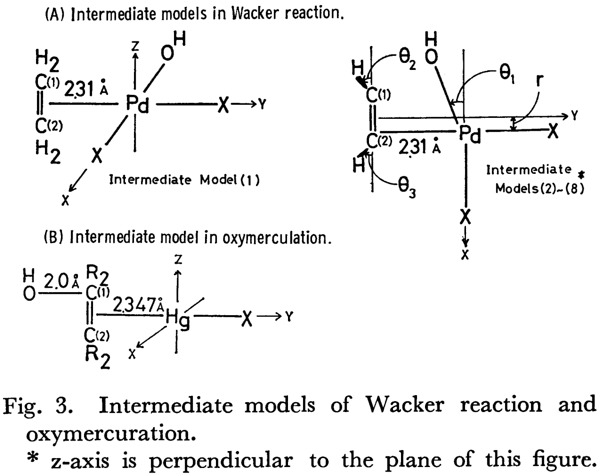


Fig. 3. Intermediate models of Wacker reaction and oxymercuration.
* z-axis is perpendicular to the plane of this figure. Intermediate Model **2**; r=0.0 Å, θ_1=0°, θ_2=0°, θ_3=0°; Model **3**; r=0.0 Å, θ_1=15°, θ_2=0°, θ_3=0°; Model **4**; r=0.0 Å, θ_1=30°, θ_2=0°, θ_3=0°; Model **5**; r=0.3 Å, θ_1=30°, θ_2=0°, θ_3=0°; Model **6**; r=0.3 Å, θ_1=30°, θ_2=7.5°, θ_3=0°; Model **7**; r=0.3 Å, θ_1=30°, θ_2=15°, θ_3=0°; Model **8**; r=0.3 Å, θ_1=30°, θ_2=15° θ_3=7.5°. Pd-O 1.92 Å

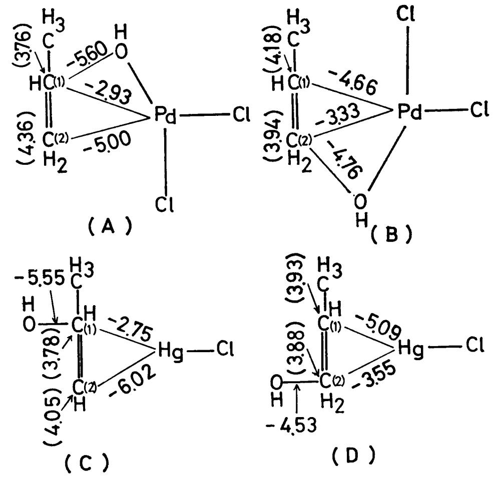


Fig. 4. The values* of $\boldsymbol{E}_{AB}$ and electron densities in Wacker reaction and oxymercuration of propylene. in parenthesis; electron density on atom. *) eV unit. Configurations A and B are the same as the intermediate model **4** in Fig. 3. Configurations C and D are the same as the intermediate model for oxymercuration in Fig. 3.

determining step. The models for these intermediates are shown in Fig. 3.

In order to investigate the selectivity in the Wacker reaction[34)] and the oxymercuration,[6)] we carried out the MO calculation of the models described in Fig. 4.

Results and Discussion

Pd(II)- and Hg(II)-ethylene Complexes. The electron densities, the π-bond order, $\boldsymbol{P}_{\pi}$,[37)] the π^*-bond order, $\boldsymbol{P}_{\pi^*}$,[37)] the quantities of transferred electrons from ethylene to metal-ligand part, $\Delta\boldsymbol{Q}$, are shown in Table 3. The electron densities on the Pd and Hg atoms increase with the decrease in the electron negativity of the halogen atom, except in the case of $HgCl(C_2H_4)^+$ or $HgBr(C_2H_4)^+$. The electron density on the C atom is decreased by the coordination as follows; free ethylene>ethylene coordinated to Pd(II)>ethylene coordinated to Hg(II). It is notable that this decreasing order agrees with the increasing reactivity for the nucleophile; *i.e.*, the nucleophilic attack of OH^- in the Wacker reaction slowly proceeds,[31–35)] and that in the oxymercuration proceeds very fast,[38)] while the reaction can not occur in the absence of Pd(II) and Hg(II).

TABLE 3. THE ELECTRONIC STRUCTURES OF Pd(II)- AND Hg(II)-ETHYLENE COMPLEXES

Compound	Electron density Metal			$\boldsymbol{P}_{\pi}$ a)	$\boldsymbol{P}_{\pi^*}$ b)	$\Delta\boldsymbol{Q}$ c)
	d	*sp*	Carbon			
C_2H_4			4.133	1.000	0.0	0.0
$PdF_3(C_2H_4)^-$	8.076	1.418	4.083	0.884	−0.009	0.240
$PdCl_3(C_2H_4)^-$	8.015	2.014	4.080	0.870	−0.012	0.252
$PdBr_3(C_2H_4)^-$	7.975	2.164	4.078	0.864	−0.013	0.259
$Hg(C_2H_4)^{2+}$	9.983	0.751	3.974	0.654	−0.002	0.734
$HgF(C_2H_4)^+$	9.931	1.010	4.050	0.806	−0.003	0.429
$HgCl(C_2H_4)^+$	9.942	1.282	4.044	0.807	−0.003	0.426
$HgBr(C_2H_4)^+$	9.944	1.376	4.045	0.813	−0.003	0.414

a) π-Bond order of the C=C double bond. b) See the footnote (37). c) The quantity of transferred electron from olefin to metal.

TABLE 4. THE COORDINATION BOND ORDERS OF Pd(II)- AND Hg(II)-ETHYLENE COMPLEXES

Compound	π-acceptor $\boldsymbol{P}_{d\pi-\pi^*}$ a)	σ-donor $\boldsymbol{P}_{d\sigma-\pi}$	$\boldsymbol{P}_{s-\pi}$	$\boldsymbol{P}_{p\sigma-\pi}$
$PdF_3(C_2H_4)^-$	0.131	0.235	0.256	0.282
$PdCl_3(C_2H_4)^-$	0.144	0.267	0.232	0.310
$PdBr_3(C_2H_4)^-$	0.147	0.273	0.229	0.319
$Hg(C_2H_4)^{2+}$	0.062	0.088	0.630	0.201
$HgF(C_2H_4)^+$	0.072	0.115	0.439	0.294
$HgCl(C_2H_4)^+$	0.060	0.110	0.327	0.259
$HgBr(C_2H_4)^+$	0.074	0.104	0.370	0.344

a) $\boldsymbol{P}_{d\pi-\pi^*}$ represents the bond order matrix element between d_{π} orbital of metal and π^*-MO of ethylene, and the others such as $\boldsymbol{P}_{d\sigma-\pi}$, *etc.*, represent similar bond order matrix elements.

The values of $\Delta\boldsymbol{Q}$ in the Hg(II)-complexes are larger than those in the Pd(II)-complexes, while the values of $\boldsymbol{P}_{\pi}$ and $\boldsymbol{P}_{\pi^*}$ are smaller than those in the Pd(II)-complexes. The coordination bond orders are shown in Table 4. The π-acceptor bond orders, $P_{d\pi-\pi^*}$, in the Pd(II)-complexes are greater than those in the Hg(II)-complexes; this agrees with the larger values of $\boldsymbol{P}_{\pi^*}$ in the Pd(II)-complexes relative to those values in the Hg(II)-complexes. While in Pd(II)-complexes the contributions of the d-orbitals are remarkably large, their contributions are very small in the Hg(II)-complexes, in which the 6s and 6p orbitals of Hg(II) mainly contribute to the coordination bond. The small contribution of the 5d atomic orbitals of Hg(II) is considered to be due to the $5d^{10}$ configuration of Hg(II) as well as Ag(I)-ethylene complexes.[10b,39)]

The Oxymercuration. The results are given in Fig. 2. It may be seen from a comparison of the total energy that the *cis*-attack system is more stable than the *trans*-attack system. The absolute value of $\boldsymbol{E}_{C-O}$ in the *cis*-attack system is smaller than that in the *trans*-attack system, probably because of the interaction of the O atom with the Hg atom in the *cis*-attack system, while there is no interaction between the O and Hg atoms in the *trans*-attack system. On the other hand, the bonding interaction between the O and Hg atoms contributes to the larger stabilization of the *cis*-attack system, suggesting that the mercurinium ion is stabilized by the coordination of the nucleophile. Our results agree with the mechanism proposed by Bach *et al.*:[29)] (a) if the concentration of the nucleophile is sufficient, or if the solvent coordinates to Hg(II) to interfere with the coordination of the nucleophile, the *trans*-attack may occur, since the nucleophile in the *trans*-position interacts with the C atom of olefin more strongly than that in the *cis*-position; and (b) the mercurinium ion which is formed from a strained olefin, such as norbornene, is relatively short-lived and is

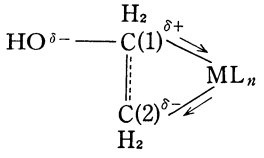
Table 5. The nucleophilic attack of OH^- to olefin coordinated to Hg(II)

Reaction system	Electron density			E_{C-O} b)	$E_{C-O}{}^{(1)}$	$E_{C-O}{}^{(2)}$	$E_{C-O}{}^{(3)}$	$E_{Hg-C(1)}$	$E_{Hg-C(2)}$
	Metal	C(1) a)	C(2)						
$C_2H_4 \leftarrow OH^-$		3.914	4.290	−3.013	−1.961	−0.479	−0.572		
$Hg(C_2H_4)^{2+} \leftarrow OH^-$	11.599	3.944	3.836	−5.427	−3.548	−1.672	−0.207	−2.540	−3.870
$HgCl(C_2H_4)^+ \leftarrow OH^-$	11.506	3.894	4.013	−4.936	−3.051	−1.277	−0.607	−3.157	−5.788
$PdCl_3(C_2H_4)^- \leftarrow OH^-$ c)	10.114	3.851	4.105	−3.832	−2.243	−0.617	−0.972	−2.206	−5.254
HgCl(*trans*-2-C_4H_8)$^+ \leftarrow OH^-$	11.586	3.807	3.910	−5.169	−2.935	−1.081	−1.153	−3.193	−5.319
HgCl(*cis*-2-C_4H_8)$^+ \leftarrow OH^-$	11.588	3.806	3.907	−5.172	−2.931	−1.078	−1.163	−3.192	−5.310

a) See Fig. 3—c. b) The $\boldsymbol{E}_{AB}$ value of bond C(1)-O (eV unit). c) The relative position of OH^- to ethylene is the same as that in $Hg(C_2H_4)^{2+} \leftarrow OH^-$ system.

likely to react with the intimate nucleophile coordinated the mercurinium ion nearest to the olefin, since there is a remarkable bonding interaction between the C and O atoms, though this interaction is weak relative to that in the *trans*-attack system. In this case, the *cis*-attack may occur preferably.

The calculated results of the models in Fig. 3 are given in Table 5, together with the results on the interaction of OH^- with free ethylene and on the interaction of OH^- with the ethylene coordinated to the $PdCl_3^-$ anion.[40] The values of $\boldsymbol{E}_{C-O}$[41] are negative in all cases, suggesting a bonding interaction between the C atom of ethylene and the O atom of OH^-. The absolute values of $\boldsymbol{E}_{C-O}$ increase in the following order; free ethylene$<PdCl_3(C_2H_4)^-<HgCl(C_2H_4)^+<Hg(C_2H_4)^{+2}$. Those results suggest that the nucleophilic attack of OH^- on ethylene is accelerated by Pd(II) and Hg(II), and that the acceleration by Hg(II) is larger than that by Pd(II), which agrees well with the catalytic behaviour of Hg(II)[38] and Pd(II).[35] Compared with the absolute values of $\boldsymbol{E}_{C-O}{}^{(1)}$, $\boldsymbol{E}_{C-O}{}^{(2)}$, and $\boldsymbol{E}_{C-O}{}^{(3)}$ in $C_2H_4 \rightarrow OH^-$ system, those of $\boldsymbol{E}_{C-O}{}^{(1)}$ and $\boldsymbol{E}_{C-O}{}^{(3)}$ are largely increased in the $PdCl_3(C_2H_4)^- \leftarrow OH^-$ system, and the values of $\boldsymbol{E}_{C-O}{}^{(1)}$ and $\boldsymbol{E}_{C-O}{}^{(2)}$ are also increased in the $Hg(C_2H_4)^{+2} \leftarrow OH^-$ and $HgCl(C_2H_4)^+ \leftarrow OH^-$ systems. Since $\boldsymbol{E}_{AB}{}^{(1)}$ and $\boldsymbol{E}_{AB}{}^{(2)}$ indicate approximately the contribution of covalent interaction to the total energy, the existence of Hg(II) and Pd(II) may cause an increase in the covalent bonding ability of ethylene with OH^-. From the results that the electron density on the C atom in ethylene complexes decreases in the following order; free ethylene $> PdX_3(C_2H_4)^- > HgX(C_2H_4)^+ > Hg(C_2H_4)^{+2}$, the absolute values of $\boldsymbol{E}_{C-O}{}^{(3)}$ can be effected to this order, since $\boldsymbol{E}_{C-O}{}^{(3)}$ represents approximately the electrostatic energy and since the O atom has a negative charge. However, the absolute values of $\boldsymbol{E}_{C-O}{}^{(3)}$ increase in the following order: $Hg(C_2H_4)^{+2} \leftarrow OH^- < C_2H_4 \leftarrow OH^- < HgCl(C_2H_4)^+ \leftarrow OH^- < PdCl_3(C_2H_4)^- \leftarrow OH^-$; this trend disagrees with the decreasing trend of electron density on the ethylene carbon atom in the Hg(II)- and Pd(II)-ethylene complexes. This disagreement is a result of the difference in the polarization of the ethylene part between the Pd(II)- and Hg(II)-systems (see Table 5). The π-acceptor bond contributes to the coordination bond in the Pd(II)-ethylene complex, while it scarcely contributes in the Hg(II)-ethylene complex. Therefore, the electron transfer shown in Scheme 1 is more feasible in Pd(II)-complexes than in Hg(II)-complexes, which leads to a higher polarization, a smaller electron density on the C(1) atom, and a larger absolute value of $\boldsymbol{E}_{C-O}{}^{(3)}$ in the Pd(II)-complexes than in the Hg(II)-complexes. Therefore, the trend of $\boldsymbol{E}_{C-O}{}^{(3)}$ the is not same as that of the electron density of the C atom in the Pd(II)- and Hg(II)-complexes. That is, the high catalytic activity of Hg(II) is not due to the electrostatic energy, while it is probably important in the long-range interaction.



Scheme 1

In the above Scheme, M and L represent a metal and ligand respectively and "→" indicates the direction of electron transfer.

The absolute value of $\boldsymbol{E}_{C-O}{}^{(3)}$ in the $HgCl(2\text{-}C_4H_8)^+$ system is remarkably large, probably because of the larger positive charge on the olefinic carbon atom of butene coordinated to Hg(II).[42] In these cases, the polarization is small.

When the mercurinium ion has an anion ligand, the absolute value of $\boldsymbol{E}_{C-O}$ is smaller than that of the system containing no anion ligand.

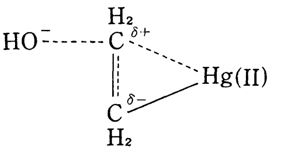
The absolute values of $\boldsymbol{E}_{C-O}$ for various reactants increase in the following order (Table 5, 8); C(β) atom of $CH_3CH{=}CH_2 < C_2H_4 <$ *trans*-2-$C_4H_8 <$ *cis*-2-$C_4H_8 <$ C(α) atom of $CH_3CH{=}CH_2$ in HgCl(olefin)$^+ \leftarrow OH^-$ system. The rate constants for the oxymercuration have been reported to increase in the following order;[38] *trans*-2-$C_4H_8 < C_2H_4 <$ *cis*-2-$C_4H_8 < CH_3CH{=}CH_2$. Our results do not agree with this order. However, it has been shown by our calculation that the reactivity of *cis*-2-C_4H_8 is higher than that of *trans*-2-C_4H_8.

The results given in Table 5 reveal the following aspect of the structure of the intermediate in the oxymercuration; (1) The electron density on the C(1) atom is larger than that on the C(2) atom except in the case of $Hg(C_2H_4)^{+2} \leftarrow OH^-$. (2) The absolute value of $\boldsymbol{E}_{Hg-C(1)}$ is larger than that of $\boldsymbol{E}_{Hg-C(2)}$. These situations are shown in the following Scheme, which agrees well with the situation usually assumed.[7]

TABLE 6. THE ELECTRONIC STRUCTURES OF INTERMEDIATE MODELS[a] IN WACKER REACTION

Intermediate			1	2	3	4	5
E_{total}[b]	F		−2581.5	−2581.5	−2582.7	−2583.0	−2593.7
	Cl		−2234.5	−2234.5	−2235.7	−2234.2	−2235.7
	Br		−2125.7	−2125.8	−2126.9	−2127.3	−2129.4
Electron density on Pd	F		9.563	9.562	9.541	9.537	9.518
	Cl		9.890	9.882	9.871	9.894	9.933
	Br		9.968	9.956	9.949	9.965	10.015
Electron density on Pd	F	C (1)	4.084	4.085	4.027	3.890	3.358
		C (2)	4.084	4.086	4.147	4.325	4.403
	Cl	C (1)	4.081	4.084	4.026	3.884	3.808
		C (2)	4.081	4.085	4.147	4.323	4.406
	Br	C (1)	4.077	4.079	4.022	3.883	3.808
		C (2)	4.077	4.085	4.146	4.323	4.400
$E_{C(1)-O}$[b]	F		0.346	0.379	−0.245	−5.321	−16.083
	Cl		0.327	0.378	−0.225	−5.212	−11.217
	Br		0.249	0.302	−0.229	−5.266	−11.330
F	$E_{Pd-C(1)}$[b]		−3.935	−3.922	−3.536	−2.818	−0.027
	$E_{Pd-C(1)}$		−3.935	−3.960	−4.203	−5.251	−6.713
Cl	$E_{Pd-C(1)}$		−3.901	−3.910	−3.670	−3.055	−1.935
	$E_{Pd-C(1)}$		−3.901	−3.876	−3.979	−4.668	−6.377
Br	$E_{Pd-C(1)}$		−3.873	−3.860	−3.549	−3.097	−2.007
	$E_{Pd-C(2)}$		−3.873	−3.894	−3.971	−4.592	−6.277
E_{Pd-O}[b]	F		−16.928	−16.859	−15.492	−15.246	−13.653
	Cl		−15.493	−15.451	−15.224	−13.848	−12.335
	Br		−15.266	−15.235	−14.978	−13.717	−10.324
P_{π}[c]	F		0.888	0.888	0.878	0.730	0.527
	Cl		0.878	0.878	0.873	0.727	0.513
	Br		0.873	0.871	0.867	0.722	0.504

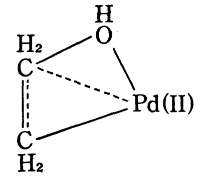
a) See Fig. 3. b) eV unit. c) π-Bond order of the C=C double bond.



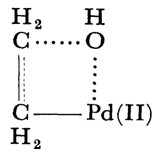
Scheme 2

In the above Scheme, "——" and "----" represent the strong interaction and the weak one respectively.

Wacker Reaction. The calculated results on intermediate models **1**—**5** are given in Table 6. From the intermediate **1** to the intermediate **5**, the values of E_{total} and E_{C-O} decrease gradually; this shows the increases in the stability of the intermediate models and in the strength of the C(1)–O bond. These results suggest that this reaction model is reasonable for the Wacker reaction. The electron densities on the Pd and C(1) atoms decrease in the course of this, while that of the C(2) atom increases. From the above results, ethylene can be said to be polarized by the approach of OH^-. Proceeding from the intermediate **1** to the intermediate **5**, the absolute values of $E_{Pd-C(1)}$, E_{Pd-O}, and P_{π} decrease, whereas that of $E_{Pd-C(2)}$ increases; *i.e.*, the bonds of C(1)–O and Pd–C(2) become stronger, although the bonds of Pd–C(1), Pd–O, and C–C become weaker, relative to those of the **1** intermediate. These results, pictured in Scheme 3, agree with the *cis*-type four-center reaction speculated by Henry[32] and Jira *et al.*[33] (see Scheme 4.)



Scheme 3



Scheme 4

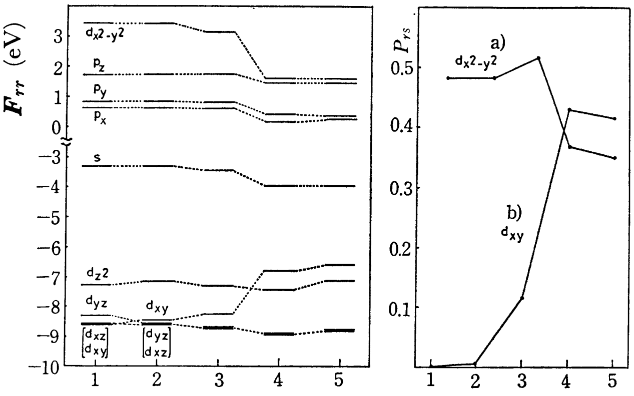
The results for the intermediate models **5**—**8** (Fig. 3) are given in Table 7. The bending of protons about C(1) makes the total energy more negative, suggesting that the system is more stabilized and that the C(1) atom changes from sp^2 to sp^3. Also, this bending brings about decreases in the absolute values of $E_{Pd-C(1)}$ and

TABLE 7. THE *cis*-BENDING OF PROTONS OF INTERMEDIATES[a] IN THE WACKER REACTION OF $PdCl_2(C_2H_4)OH$

Intemediate	5	6	7	8
E_{total}[b]	−2235.7	−2235.7	−2238.6	−2235.2
$E_{C(1)-O}$[b]	−11.22	−12.59	−13.68	−13.89
$E_{Pd-C(1)}$[b]	−1.94	−1.87	−1.83	−1.74
$E_{Pb-C(2)}$[b]	−6.38	−6.43	−6.14	−6.87
E_{Pd-O}[b]	−12.34	−12.26	−11.92	−12.00
P_{π}	0.513	0.491	0.475	0.443

a) See Fig. 3. b) eV unit.

$\boldsymbol{P}_\pi$ and increases in the absolute values of $\boldsymbol{E}_{C(1)-O}$ and $\boldsymbol{E}_{Pd-C(1)}$, which reveal that the reaction more proceeds from the intermediate **5**. However, the bending of the C(2)-H bond destabilizes the system, whereas the absolute values of $\boldsymbol{E}_{C(1)-O}$ and $\boldsymbol{E}_{Pd-C(2)}$ are increased and those of $\boldsymbol{E}_{Pd-C(1)}$ and $\boldsymbol{P}_\pi$ are decreased. Therefore, any *cis*-bending of the protons about the C(2) atom hardly occurs. These results are considered to be due to the polarization of ethylene, which is expected to be enhanced by the π-acceptor bond with Pd(II), as has been shown in Scheme 1; the C(2) atom should have sp^2 character to obtain the electron through the π-acceptor bond, leading to no *cis*-bending of its proton.



Intermediate models (A) The changes of $\boldsymbol{F}_{rr}$

Intermediate models (B) The changes of *B* and orders

Fig. 5. The changes of values of $\boldsymbol{F}_{rr}$ and bond order. a) The sum of bond orders between $d_{x^2-y^2}$ of Pd atom and s, p_x, p_y orbitals of O atom. b) The sum of bond orders between d_{xy} of Pd atom and s, p_x, p_y orbitals of O atom.

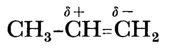
Then, the changes from the intermediate **1** to the intermediate **5** were investigated in detail. The values of the Fock-matrix elements, $\boldsymbol{F}_{rr}$, are shown in Fig. 5-A, together with the sum of the values of the density matrix elements between the $d_{x^2-y^2}$ orbital of the Pd atom and the s, p_x and p_y orbitals of the O atom, and those between the d_{xy} orbital and the s, p_x, and p_y orbitals of these atoms (Fig. 5-B). There is a remarkable increase in the value of $\boldsymbol{F}_{d_{xy}d_{xy}}$ and a decrease in the value of $\boldsymbol{F}_{d_{x^2-y^2}d_{x^2-y^2}}$, while there are few changes in the other $\boldsymbol{F}_{rr}$. These remarkable changes are due to the moving of OH^- in the xy plane and suggest the change in the Pd–O bonding character. As is shown in Fig. 3-B, the contribution of the d_{xy} orbital to the Pd-O bond increases, although that of $d_{x^2-y^2}$ decreases in the reaction course. In other words, OH^- attacks the C(1) atom, interacting with the d_{xy} orbital, as has been proposed by Cossee *et al.*[9,43)]

Markovnikoff Rule in These Reactions. We calculated the MO's of the models for the nucleophilic attack on propylene; the results are given in Fig. 4 and Table 8. In both the Pd(II)- and Hg(II)-systems, attack on the C(1) atom gives a lower total energy than the attack on the C(2) atom, which reveals that the former attack is superior to the latter attack. Also, the absolute values of $\boldsymbol{E}_{C(1)-O}$ of models [A] and [C] are greater than those of models [B] and [D]. It is obvious from Table 8 that this difference is a result of the difference of $\boldsymbol{E}_{C-O}^{(3)}$, suggesting that this selectivity is determined by the electrostatic energy. The carbon atom attacked by OH^- is positively charged in both Pd(II)- and Hg(II)-systems(see Tables 5 and 6 and Fig. 4), and the propylene is polarized by the hyperconjugation of the methyl group, as follows,

TABLE 8. NUCLEOPHILIC ATTACK OF OH^- TO PROPYLENE

State[a)]	$PdCl_2(OH)(C_3H_6)^-$ A	$PdCl_2(OH)(C_3H_6)^-$ B	$HgCl(C_3H_6)^+\leftarrow OH^-$ C	$HgCl(C_3H_6)^+\leftarrow OH^-$ D
$\boldsymbol{E}_{total}$[b)]	−2426.6	−2426.3	−2353.0	−2352.6
$\boldsymbol{E}_{C-O}$[b)]	−5.596	−4.756	−5.545	−4.528
$\boldsymbol{E}_{C-O}^{(1)}$[b)]	−3.674	−3.793	−3.063	−2.923
$\boldsymbol{E}_{C-O}^{(2)}$[b)]	−0.618	−0.660	−1.175	−1.185
$\boldsymbol{E}_{C-O}^{(3)}$[b)]	−1.305	−0.303	−1.307	−0.420
$\boldsymbol{P}_\pi$	0.669	0.718	0.531	0.535

a) See Fig. 4. b) eV unit.



$$CH_3\text{-}\overset{\delta+}{CH}\text{=}\overset{\delta-}{CH_2}$$

Scheme 5

Therefore, the attack on the C(α) atom is superior to the attack on the C(β) atom, since the former attack causes the same polarization, while the latter attack causes an inverse polarization.

As has been described above, the semi-empirical SCF-MO method using the modified CNDO approximation gives fruitful results; this encourages us to apply this method to studies of the other catalytic reactions.

The calculations were carried out by means of the FACOM 230—60 Computer in the Data Processing Center at Kyoto University.

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$$\boldsymbol{P}_\pi = 2\sum_{\pi}^{\mathrm{occ}} C_{\pi^1 \mathrm{p_y}} C_{\pi^2 \mathrm{p_y}}$$

$$\boldsymbol{P}_{\pi^*} = 2\sum_{\pi^*}^{\mathrm{occ}} C_{\pi^{*1} \mathrm{p_y}} C_{\pi^{*2} \mathrm{p_y}}$$

where $C_{\pi^1 \mathrm{p_y}}$ and $C_{\pi^{*1} \mathrm{p_y}}$ represent the MO coefficients of $\mathrm{p_y}$ orbital on C(1) atom in π-MO and π^*-MO respectively.

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40) Although OH^- is considered to attack to ethylene as shown in Fig. 3, the *trans*-attack model is calculated in this case for comparison with the oxymercuration.

41) These $\boldsymbol{E}_{\mathrm{C-O}}$ and $\boldsymbol{E}_{\mathrm{C-O}}^{(1)}$ *etc.*, represent the value of $\boldsymbol{E}_{\mathrm{AB}}$ and $\boldsymbol{E}_{\mathrm{AB}}^{(1)}$ *etc.*, of bond C(1)-O, respectively (in eV unit and see Fig. 3).

42) In Hg(II)-complexes, the unsaturated C atom of 2-C_4H_8 has a smaller electron density than that of C_2H_4; *i.e.*, 3.993 in HgCl(*cis*-2-C_4H_8)$^+$, 3.995 in HgCl(*trans*-2-C_4H_8)$^+$ and 4.048 in HgCl(C_2H_4)$^+$.

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