JOURNAL OF CATALYSIS 39, 294–297 (1975)

NOTES

An Extended Hückel Molecular Orbital Study of the Acetoxylation of Propylene over Palladium Metal and Salts Catalysts

Acetoxylation of olefins catalyzed by palladium ion in solutions has been reported (*1*). However, the reaction by palladium metal catalysts is not yet studied sufficiently, and the reaction scheme for allylic products has not fully been elucidated.

In order to clarify the difference between the catalytic activities of palladium metal and salts, we previously attempted to acetoxylate propylene in the gas phase with both catalysts under the same reaction conditions (*2*). We found that over palladium salt catalysts propylene gives acetone and allyl acetate, the former being formed by secondary hydrolysis of isopropenyl acetate, while over palladium metal catalyst propylene gives allyl acetate selectively as indicated in Table 1.

In this paper, the mechanism of acetoxylation catalyzed by palladium metal or palladium salts is discussed from the view point of the extended Hückel molecular orbital theory.

Method of calculation. The LCAO-MO procedure employed in this study is a modification of the extended Hückel molecular orbital theory used by Hoffmann (*3*). As is usually done in the extended Hückel method, the diagonal matrix elements (Hii) were approximated by valence-state ionization potentials (VSIP) as shown in Table 2. The off-diagonal terms were given as $Hij = KSij(Hii + Hjj)/2$ ($K = 1.75$). The overlap integrals are calculated from the formulas for Slater-type orbitals, using atomic-orbital exponents (μ) as prescribed by Burns (*4*). The diagonal terms (Hii) were calculated iteratively using the method of Rein *et al.* (*5*). This method assumes a linear dependence of the ionization potential on the net atomic charge q, as expressed by $Hii = Hii\ (0) - q\Delta\alpha$. The orbital exponents of each iteration were adjusted for the charge on the atom according to $\mu = \mu^0 + (0.135/n)$, where μ^0 and μ are the exponents for orbitals on the neutral and charged atom, respectively. This is merely an extension of Slater's rules, where n is the effective principal quantum number. Iterations were continued until the atomic charges became constant for every atom to within 0.02 electronic charge.

TABLE 1

CONVERSION AND PRODUCT DISTRIBUTION IN ACETOXYLATION OF PROPYLENE[a]

		Product distribution (%)			
Catalyst[b]	Conversion (%)	Isopropenyl acetate	Acetone	Allyl acetate	Others
$PdCl_2$–AC	8.6	0	73	27	0
$Pd(NO_3)_2$–AC	4.4	0	79	20	1[c]
$PdSO_4$–AC	3.1	0	68	27	6[c]
$Pd(OAc)_2$–AC	3.0	5	49	43	3[d]
Pd-γ-Al_2O_3	3.6	0	0	89	11[e]
Pd–AC	3.5	3	2	92	3[e]

[a] Fixed-bed reactor. Reaction conditions: $W/F = 10.0$ g-cat hr/mol, 135°C. Feed ratio: propylene:oxygen:acetic acid = 5:2:5.

[b] Palladium salts supported on activated carbon (AC). Palladium metal supported on activated carbon or γ-alumina.

[c] Isopropyl acetate.

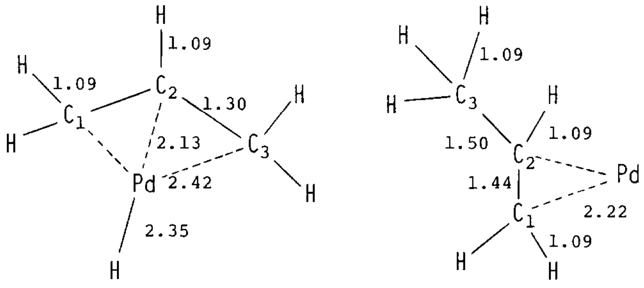
[d] n-Propenyl acetate.

[e] Diacetate compounds.

TABLE 2
INPUT PARAMETERS FOR THE ATOMS

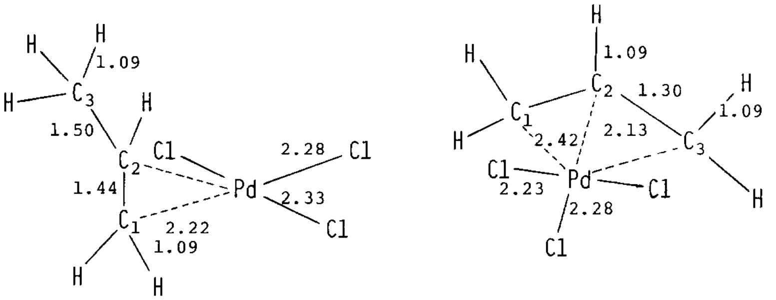
Orbital	Hydrogen 1s	Carbon 2s	Carbon 2p	Chlorine 3s	Chlorine 3p	Palladium 5s	Palladium 5p	Palladium 4d
Hii (eV)	−13.60	−21.43	−11.42	−25.23	−13.34	−7.60	−3.84	−12.02
$\Delta\alpha$ (eV)	14.00	11.90		14.20			6.90	
μ	1.200	1.550	1.325	2.183	1.733	1.675	0.900	3.068

Structural parameters. Bond lengths and angles were taken from the X-ray structure analyses of $Pd_2Cl_2(allyl)_2$ (*6*) and $[PdCl_2(C_2H_4)]_2$ (*7*). The X, Y plane was defined by the π-allyl group and π-complex, respectively. The Z axis perpendicular to the X, Y plane shows the direction of these π-electron orbitals. In order to determine the geometries of adsorption on palladium metal and salt, the total electron energies of π-allyl complex with Pd (**I**), π-complex with Pd (**II**), π-complex with $PdCl_3$ (**III**), and π-allyl complex with $PdCl_3$ (**IV**) were calculated by extended Hückel method. The coordinate systems used for the calculations are shown in Fig 1. The values of total electron energies of (**I**), (**II**), (**III**), and (**IV**) were calculated as −448.55, −444.07, −784.24 and −775.29 eV. These results indicate that propylene reacts with palladium metal to form π-allyl complex by abstraction of hydrogen of the methyl group rather than simple π-complex as the reaction intermediate since the total electron energy of (**I**) is lower than that of (**II**) and that propyl-



(I) π-allyl complex with Pd.

(II) π-complex with Pd.



(III) π-complex with $PdCl_3$.

(IV) π-allyl complex with $PdCl_3$.

FIG. 1. The molecular structure used for the calculation on the π-allyl complex with Pd (**I**), π-complex with Pd (**II**), π-complex with $PdCl_3$ (**III**), and π-allyl complex with $PdCl_3$ (**IV**) (all numbers in Å).

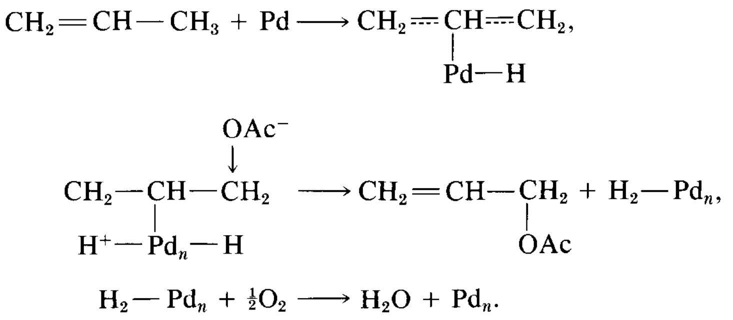
TABLE 3
Molecular Orbitals for π-Allyl System

	Atomic charge[a]	Atomic orbital population		
		π_b −15.260 eV	π_n −10.048 eV	π_a −0.593 eV
C_1	+0.371	0.1070	0.5029	0.5384
C_2	−0.065	0.2629	0.0	1.0942
C_3	+0.371	0.1070	0.5029	0.5384
Pd	+0.021			
H	−0.664			

[a] Population analysis [from R. S. Mulliken, *J. Chem. Phys.* **23**, 1833, 1841 (1955)].

ene reacts with palladium salt to form π-complex rather than π-allyl complex by abstraction of hydrogen since the total electron energy of **(III)** is lower than that of **(IV)**. Therefore, the atomic orbital populations of π-electron orbitals of complex **(I)** and **(III)** are discussed in detail.

π-Allyl complex. As in the simple Hückel method (*6*), three molecular orbitals described below are formed in a three-center arrangement of carbon atoms for the π-allyl palladium complex by this extended Hückel calculation: one occupied bonding orbital (π_b) involving all three carbons, one empty non-bonding orbital (π_n) with all of the electron density on the two extreme carbons, and one empty anti-bonding orbital (π_a). Since hydrogen is considered to be abstracted from propylene as hydride ion, π_n orbital is the lowest vacant orbital. The large value of electron density of π_n orbital on the extreme carbons as is shown in Table 3 leads to high reactively for nucleophilic reaction (*8*). In view of this, the nucleophilic reagent such as acetate anion reacts with one of the identical extreme carbons to give allyl acetate as a major product. This agrees well with the results shown in Table 1. It seems reasonable to consider that the hydrogen of methyl group of propylene is abstracted by palladium atom to give π-allyl complex, and the nucleophilic addition in the π-allyl complex to give allyl acetate.



$$\mathrm{CH_2{=}CH{-}CH_3 + Pd \longrightarrow CH_2{\cdots}\underset{\substack{|\\ Pd-H}}{CH}{\cdots}CH_2,}$$

$$\mathrm{CH_2{-}\underset{\substack{|\\ H^+-Pd_n-H}}{\overset{\substack{OAc^-\\ \downarrow}}{CH}}{-}CH_2 \longrightarrow CH_2{=}CH{-}\underset{\substack{|\\ OAc}}{CH_2} + H_2{-}Pd_n,}$$

$$\mathrm{H_2{-}Pd_n + \tfrac{1}{2}O_2 \longrightarrow H_2O + Pd_n.}$$

TABLE 4
Molecular Orbitals for π-Complex

	Atomic charge	Atomic orbital population	
		π_o −13.446 eV	π_e −5.596 eV
C_1	−0.037	0.1136	0.7022
C_2	0.0	0.0698	0.7606
C_3	−0.067	0.0168	0.0004
Pd	0.307		

π-Complex. Our calculation shows that two molecular orbitals are formed on carbon–carbon double bond after the coordination with palladium salts, one is the occupied bonding orbital (π_o) involving three carbons and the other is the empty antibonding orbital (π_e) (Table 4). As the difference in electron density of π_e orbital between extreme carbon 1 and middle carbon 2 is not so large, the acetate anion can react with both carbons and gives allyl acetate as well as isopropenyl acetate. Electron density of carbon 2 is, however, somewhat larger than that of carbon 1, and

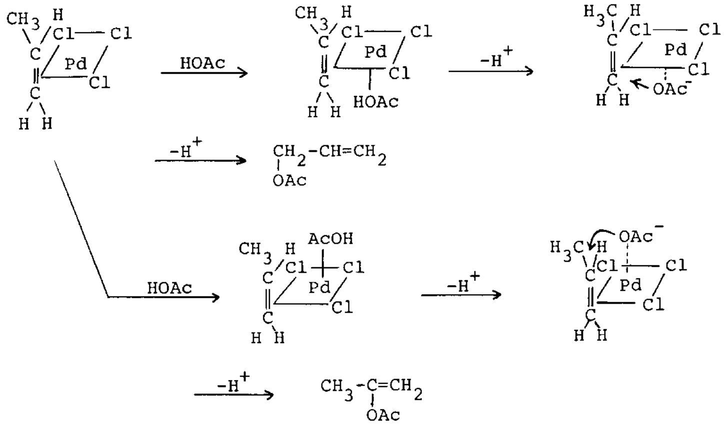


FIGURE 2.

so the amount of acetone which is formed by the hydrolysis of isopropenyl acetate (2) is larger than that of allyl acetate. The vapor phase reaction on supported palladium salts catalysts appears to follow the same reaction scheme as in the solution. This calculation supports the mechanism (Fig. 2) proposed by Stern (9).

REFERENCES

1. Kitching, W., Rappoport, Z., Winstein, S., and Young, W. G., *J. Amer. Chem. Soc.* **88,** 2054 (1966).
2. Arai, H., Kojima, S., Fujimoto, K., and Kunugi, T., *Kogyo Kagaku Zasshi* **72,** 1767 (1969); Kunugi, T., Arai, H., and Fujimoto, K., *Bull. Jap. Petrol. Inst.* **12,** 97 (1970).
3. Hoffmann, R., *J. Chem. Phys.* **39,** 1397 (1963).
4. Burns, G., *J. Chem. Phys.* **41,** 1521 (1964).
5. Rein, R., Fukuda, N., Win, H., Clarke, G. A., and Harris, F. E., *J. Chem. Phys.* **45,** 4743 (1966).
6. Green, M. L. H., and Nagy, P. L. I., "Advances in Organometallic Chemistry," Vol. 2, p. 325. Academic Press, New York, 1964.
7. Sutton, L. E., "Tables of Interatomic Distances and Configuration in Molecules and Ions." Burlington House, London, 1958.
8. Fukui, K., Yonezawa, T., and Shingu, H., *J. Chem. Phys.* **20,** 722 (1952); Fukui, K., Yonezawa, T., Nagata, C., and Shingu, H., *J. Chem. Phys.* **22,** 1433 (1954).
9. Stern, E. W., "Catalysis Reviews," Vol. 1, p. 105. Dekker, New York, 1968.

HIROMICHI ARAI
TAISEKI KUNUGI

Department of Synthetic Chemistry
Faculty of Engineering
University of Tokyo
Hongo, Bunkyo-ku
Tokyo, Japan
Received January 23, 1975