

Hydroesterification of ethylene catalyzed by Pd(II) complexes: an ab initio MO study

Michiyo Kawana, Shinichiro Nakamura*, Eiichi Watanabe, Hisao Urata

Mitsubishi Chemical Corporation Research and Development, Division Yokohama Research Center, 1000 Kamoshida-cho, Aoba-ku, Yokohama 227, Japan

Received 10 January 1996; revised 22 January 1997

Abstract

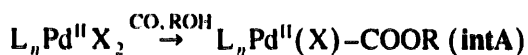
An ab initio MO study showed that hydrido-Pd species would be a preferable key intermediate instead of alkoxycarbonyl-Pd species in the Pd(II)-catalyzed hydroesterification of ethylene. © 1997 Elsevier Science S.A.

Keywords: Hydroesterification; Pd(II); Pd-H; Ab initio MO

1. Introduction

The hydroesterification reaction is one of the most important processes in homogeneously catalyzed transformations from olefins to the corresponding esters. Although many reaction conditions have been reported to achieve the present reaction [1], it has not been clear what the key intermediate of the Pd(II)-catalyzed hydroesterification is, and much attention has been focused on the mechanism. The two catalytic cycles are proposed based on the observed intermediates, they are schematically shown as Cycles A and B in Fig. 1.

The intermediate which suggests the Cycle A is alkoxycarbonyl-Pd(II) complex, shown as (intA) in Fig. 1. It is believed to be produced by the reaction [2–4]



The olefin insertion into the Pd–C bond of this intermediate (intA) and HX addition will produce the corresponding ester.

On the other hand, Cycle B is also proposed based on the hydrido-Pd(II) complex, shown as (intB) in Fig. 1. The origin of the initial generation of (intB) has not been well understood. The olefin insertion into the Pd–H bond will produce an alkyl–Pd complex, then the

following CO insertion and alcoholysis will produce the corresponding ester.

Although these two are different mechanisms, both mechanisms are supported by their key intermediates. Additionally, the fact that the presence of protons accelerates this hydroesterification has been reported independently by the Shell group and by us [5].

In an attempt to clarify which intermediate is preferable in the hydroesterification of olefin using a Pd(II) catalyst, we have carried out ab initio calculations which provide the direct information of transition states in elemental reactions. After we obtained our results of calculations, Sugita and coworkers reported the detection of the Pd–H species by the in situ IR technique in the hydroesterification of 2-acetoxypyrone catalyzed by $(Ph_3P)_2PdCl_2$ in the presence of an equimolar amount of amine [6] based on Pd. Together with this finding, the purpose of this paper is to provide a theoretical support for the PdH species (Cycle B) in the hydroesterification.

2. Method

All the calculations were carried out by an ab initio MO method¹ [7] with Dunning's double zeta contrac-

* Corresponding author.

¹ The calculations were carried out on an IBM Powerstation 550.

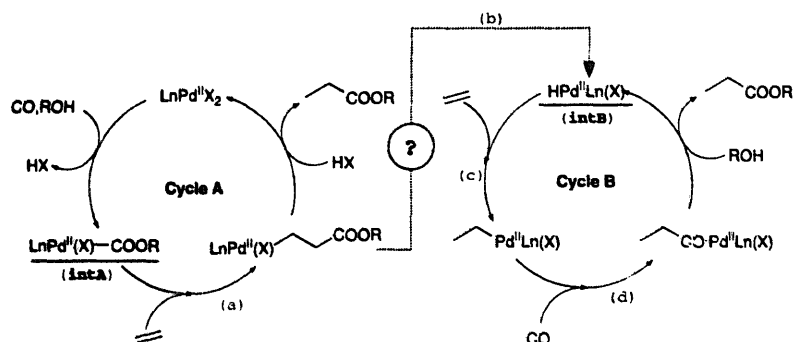


Fig. 1. Two proposed mechanisms for carboalkoxylation. (a), (b), (c) and (d) are studied in this paper.

tion of Huzinaga's primitive basis set [8] on H, C and O atoms, and the Los Alamos effective core potential together with the double zeta basis set [9] (ECP-1) on P, Cl and Pd atoms. The equilibrium and the transition state (TS) structures were determined by full geometry optimization of the analytical energy gradient method at the RHF level. All the optimized structures were verified to be the minimum or the TS through the frequency analysis. We also performed optimization by the MP2 method with ECP-1 for comparison.

Further, energies were obtained by the fourth-order Møller Plesset perturbation (MP4) method [10] with Hay's norm-conserving relativistic effective core potentials [11] (ECP-2) so that the 5s and 5p core orbitals

were explicitly included in the calculation. The olefins and PR_3 were replaced by C_2H_4 and PH_3 , respectively.

3. Results and discussions

The important elemental reactions of both Cycles A and B were investigated, then further energetics were estimated.

3.1. Elemental reactions in Cycles A and B at the RHF level

First, the olefin insertion reaction in Cycle A has been calculated, respecting the results by Toniolo and

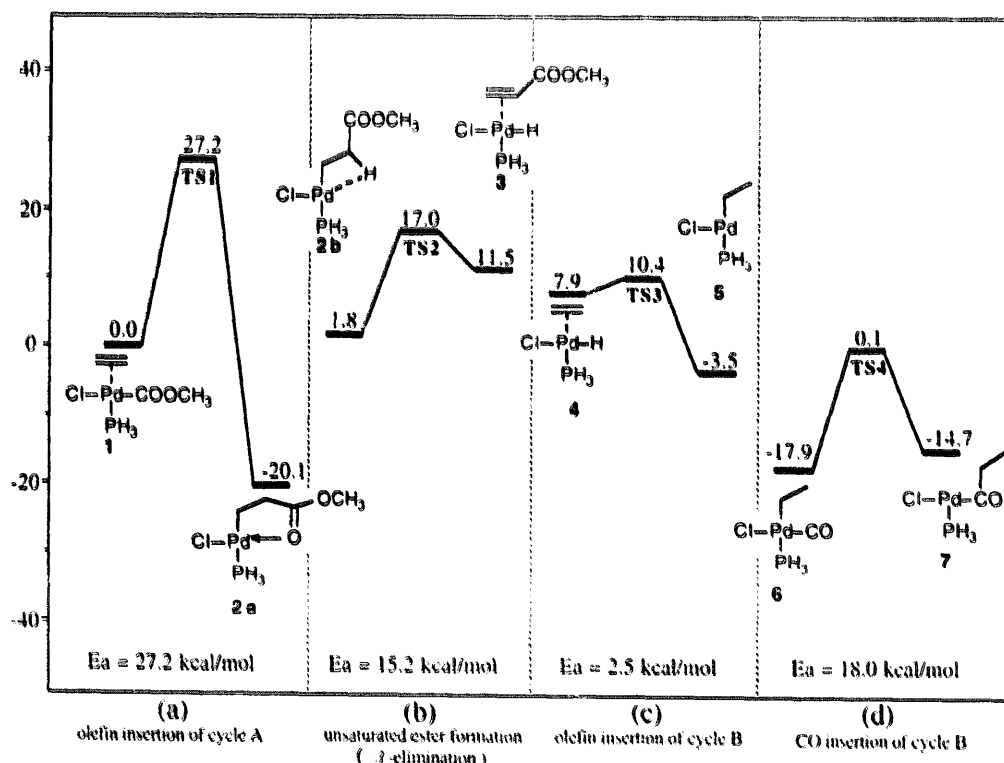


Fig. 2. The energy profile obtained at the RHF/ECPI level. The numbers taking into account the stoichiometric balance are shown in kcal mol⁻¹ (1 a.u. = 627.7 kcal mol⁻¹) relative to **1** (upright form) + C_2H_4 + CO. The calculated energies in a.u. are for **1** (upright), -357.07715, for C_2H_4 , -78.01179, for CO -112.68507 and for $CH_2CHCOOCH_3$, -304.58627.

coworkers that the hydroesterification started from Pd-carbonyls [3]. As shown in Fig. 2(a) beginning with the upright form of olefin complex (1),² The former is the minimum, but the latter is not confirmed as the minimum by the frequency analysis at the RHF level, via the TS having the energy barrier of 27.2 kcal mol⁻¹ (RHF), 2-alkylcarbonylethyl-Pd is obtained. Interestingly, the optimization has led to a stable chelate complex³ [12] (2a) in which the carbonyl oxygen coordinates on to a Pd vacant site.

Secondly, the unsaturated ester formation (2b → 3) (in Fig. 2(b)) has been calculated, reflecting the experimental evidence [13,14] of the unsaturated ester formation. The reactant 2b is stabilized by 1.1 kcal mol⁻¹ through an agostic interaction relative to the geometry without the agostic interaction. The late TS is located between 2b and the product 3 (coplanar form).⁴ The structure is shown in Fig. 3(b). The product is the hydrido complex. Consequently, the calculation has reproduced the experimental result of unsaturated ester formation [13,14]; moreover, it turns out that the possible source of the hydrido complex, the key intermediate in Cycle B, has been prepared through this β-elimination (see Section 4).

Finally, two important elemental reactions in Cycle B are calculated. First, olefin insertion (4 → 5) is shown in Fig. 2(c). Starting from the coplanar form of olefin complex,⁵ the early TS (Fig. 3(c)) is located having a very low activation energy (2.5 kcal mol⁻¹ in RHF), indicating the smooth process of the step. The second one is CO insertion reaction (6 → 7) depicted in Fig. 2(d). The reaction virtually consists of alkyl migration, being consistent with previously reported theoretical studies [15]. The obtained TS shows a considerable energy barrier of 18.0 kcal mol⁻¹. The structure is shown in Fig. 3(d).

3.2. Further energetics

The examination of the electron correlation is necessary before reaching any conclusion, since the complexes studied in this paper have a Pd-π bond of olefin, Pd-CO, and Pd-COOCH₃ bond, where a different magnitude of back donation exists in each bond. It is known that a well-balanced description of these bonds requests the consideration of the electron correlation [16,17].

² The upright form (C₂H₄ out of plane) of 1 is more stable than the coplanar form (C₂H₄ in plane) by 4.5 kcal mol⁻¹ (RHF).

³ A similar complex is reported by ³¹P{¹H} NMR (see Ref. [11]).

⁴ The coplanar form of 3 is less stable than the upright form by 1.6 kcal mol⁻¹ (RHF). Both are confirmed as the minimum.

⁵ The coplanar form of 4 is less stable than the upright form by 1.4 kcal mol⁻¹ (RHF). Both are confirmed as the minimum.

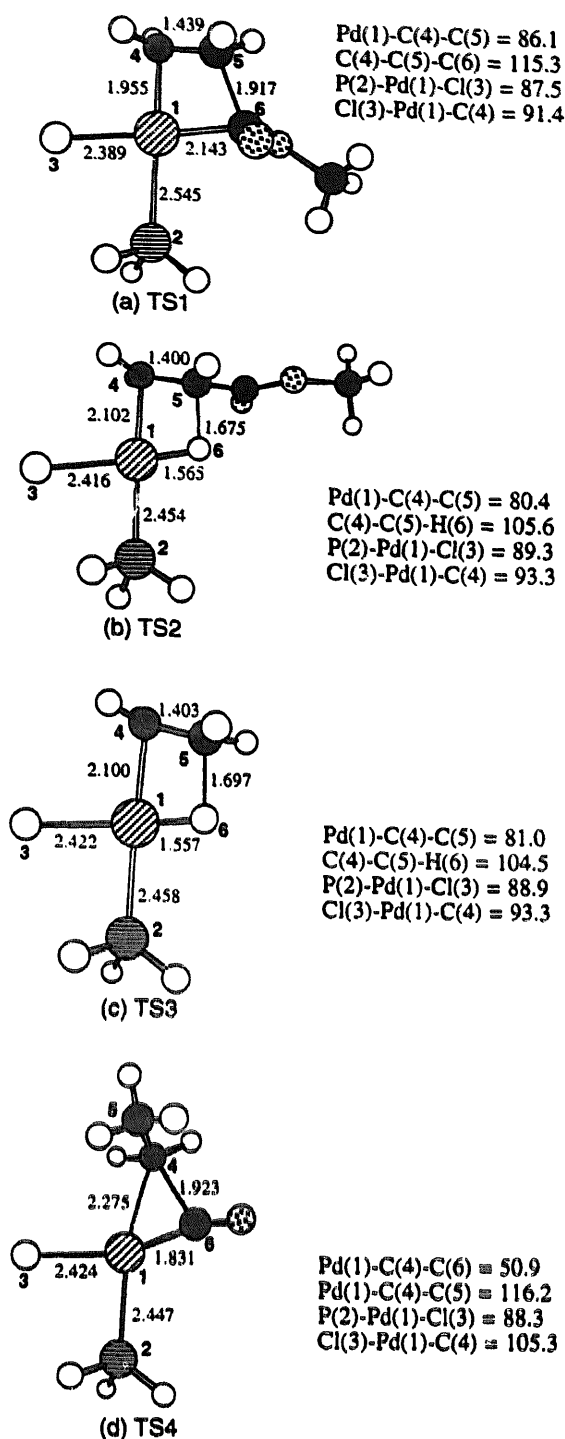


Fig. 3. Geometries (Å, deg) of TSs obtained by RHF/ECPI optimization as having only one imaginary frequency.

Then the energies by effective core potential with outermost core orbitals (ECP-2) are also obtained. The results are summarized in Table 1. The first two lines show the energy of the RHF and MP2 level. The third line shows the MP2-optimized results. The next three lines cover the energies at the RHF MP2 and MP4-SDTQ level by ECP-2.

Table 1
Relative energies (kcal mol⁻¹) at various level of calculation

Method	1	TS1	2a	2b	TS2	3	4	TS3	5	6	TS4	7
RHF/ECPI	0.0	27.2	-20.1	1.8	17.0	11.5	7.9	10.4	-3.5	-17.9	0.1	-14.7
MP2/ECPI//RHF/ECPI	0.0	14.8	-6.5	8.6	16.2	18.4	19.6	17.7	7.1	-23.2	-8.8	-4.2
MP2/ECPI	0.0	17.4	-3.9	8.3	17.1	14.6	16.9	17.3	5.7	-26.1	-6.4	-7.4
RHF/ECPI2//RHF/ECPI	0.0	29.5	-19.2	0.7	14.5	3.3	-0.3	7.2	-4.8	-17.3	1.3	-16.1
MP2/ECPI2//RHF/ECPI	0.0	18.1	-5.2	8.2	12.4	8.7	8.4	10.7	4.3	-24.1	-10.9	-7.4
MP4-SDTQ/ECPI2//RHF/ECPI	0.0	20.0	-4.5	10.7	14.4	9.8	10.0	13.0	7.2	-24.1	-10.6	-7.6

'/' and '//' mean 'with the basis set of' and 'at the structure optimized with' respectively. For instance MP2/ECPI//RHF/ECPI indicates the MP2 energy calculation with the basis set ECP2 at the structure optimized by the RHF calculation using the basis set ECPI.

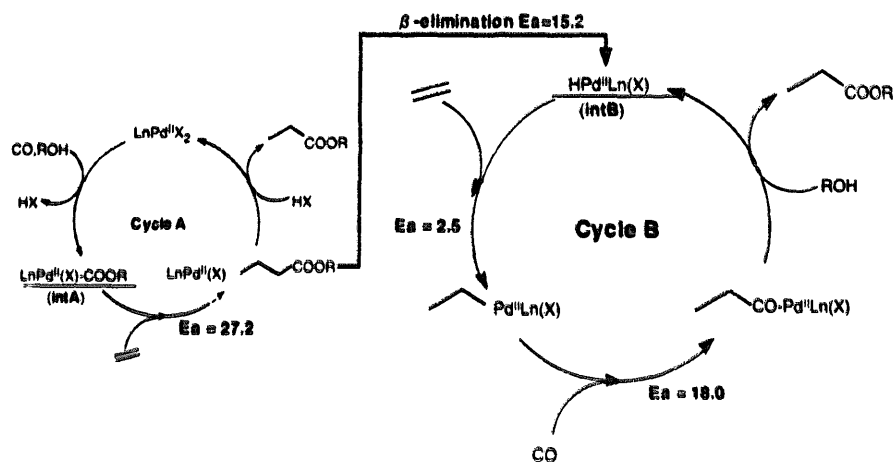


Fig. 4. The conclusion of this study. Activation energies E_a /kcal mol⁻¹.

The most critical modification was brought about by advancing from RHF to MP2 level, the TS2 and TS4 had disappeared (see the second line of Table 1). However, as shown in the third line, by optimizing again at the MP2 level, this was corrected (see the third line). By adopting the ECP-2, the TS4 had disappeared advancing from RHF to MP2, MP4-SDTQ level. The correction may be obtained by the geometry optimization of these levels, as occurred above (in ECP-1). Although the absolute values shifted, the remaining energy profile supported the global picture as shown in Fig. 2.

4. Conclusion

Based on this theoretical study, the hydrido-Pd (Pd-H) species (IntB of Cycle B) would be a more preferable key intermediate than the alkoxy-carbonyl-Pd (Pd-COOR) species (IntA of Cycle A) in the Pd(II)-catalyzed hydroesterification of ethylene. The initial generation of the hydrido-Pd species (IntB) can now be understood, by the intervention of β -elimination from the 2-alkoxy-carbonyl-ethyl-Pd intermediate of Cycle A. This provides a reasonable explanation as to why two different mechanisms were apparently compatible previ-

ously. The final picture obtained by the current study is shown in Fig. 4.

Further study adopting the propylene as an olefin is in progress.

Acknowledgements

The authors thank Professor A. Yamamoto, Professor N. Koga and Dr. Y. Oishi for encouraging support and discussion.

References

- [1] J.P. Collman, L.S. Hegehus, J.R. Norton, R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, CA, 1987.
- [2] D. Milstein, Acc. Chem. Res. 21 (1988) 428.
- [3] G. Cabinato, L. Toniolo, J. Organomet. Chem. 398 (1990) 187.
- [4] T. Fuchikami, K. Ohishi, I. Ojima, J. Org. Chem. 48 (1983) 3803.
- [5] Japanese Patent, 1984 Kokai-59082336, Shell. Japanese Patent, 1987 Kokai-62-161737, Mitsubishi Kasei Corporation.
- [6] K. Kudo, K. Mitsuhashi, S. Mori, K. Komatsu, N. Sugita, Chem. Soc. Jpn. Chem. Lett. (1993) 1615.

- [7] M. J. Frisch, G.W. Trucks, M. Head-Gordon, P.M.W. Gill, M.W. Wong, J.B. Foresman, B.G. Johnson, H.B. Schlegel, M.A. Robb, E.S. Replogle, R. Gomperts, J.L. Andres, K. Raghavachari, J.S. Binkley, C. Gonzalez, R.L. Martin, D.J. Fox, D.J. Defrees, J. Baker, J.J.P. Stewart, J.A. Pople, Gaussian 92, Revision C.4, Gaussian, Inc., Pittsburgh, PA, 1992.
- [8] T.H. Dunning, P.J. Hay, *Modern Theoretical Chemistry*, Plenum, New York, 1976, Chapter 1, pp. 1–28.
- [9] P.J. Hay, W.R. Wadt, *J. Chem. Phys.* 82 (1985) 270. W.R. Wadt, P.J. Hay, *J. Chem. Phys.* 82 (1985) 284. P.J. Hay, W.R. Wadt, *J. Chem. Phys.* 82 (1985) 299.
- [10] C. Møller, M.S. Plesset, *Phys. Rev.* 46 (1934) 618.
- [11] P.J. Hay, *New. J. Chem.* 15 (1991) 735–740.
- [12] G.P.C.M. Dekker, C.J. Elsevier, K. Vieve, P.W.N.M. van Leeuwen, C.F. Roobeek, *J. Organomet. Chem.* 430 (1992) 357.
- [13] S. Otsuka, A. Nakamura, T. Yoshida, M. Naruto, K. Ataka, *J. Am. Chem. Soc.* 95 (1973) 3180.
- [14] R.F. Heck, *J. Am. Chem. Soc.* 94 (1972) 2712.
- [15] N. Koga, K. Morokuma, *New. J. Chem.* 15 (1991) 749 and references cited therein.
- [16] N. Koga, K. Morokuma, *Theoretical Aspects of Homogeneous Catalysis*, Dordrecht, The Netherlands, Kluwer, 1995, pp. 65–91, 93–113.
- [17] I.B. Bersuker, *Electronic Structure and Properties of Transition Metal Compounds*, Wiley, New York, 1996, pp. 603–637.