MILD ALKOXYCARBONYLATION OF OLEFINS IN THE PRESENCE OF PALLADIUM COMPLEXES

E. G. Chepaikin, A. P. Bezruchenko,
A. Benjeu, and A. Joo

UDC 542.97:547.313

Palladium complexes catalyze the carbonylation of olefins under vigorous conditions [1]. In our opinion, one of the reasons for this behavior is the presence of a halide ligand in these complexes, which inhibits the formation of catalytically active "alcoholate" or hydride intermediates [2].

We are the first to report that $Pd(PPh_3)_4$ or PdA_2—n-PPh_3 (where A is a nonhalide acido-ligand such as acetylacetonate or acetate) in conjunction with a nonhalide acid such as p-toluenesulfonic acid (PTSA) catalyzes the carbonylation of olefins in alcohol solutions at atmospheric pressure. In addition to the carbonylation of α-olefins, isomerization to β-olefins proceeds more rapidly; β-olefins are carbonylated at much lower rates.

In a typical experiment, 0.1 mmole $Pd(AcAc)_2$, 0.6 mmole PPh_3, 0.3 mmole PTSA, and 8.5 ml butanol were added to the reactor. Then, 1.06 mmole 1-decene was introduced in a CO atmosphere at 80°C. About 25% of the calculated amount of gas is absorbed over 15 min, and then the reaction rate decreases. This inhibition is related not to deactivation of the catalyst but rather with the isomerization of 1-decene to 2-decene. Upon 80% olefin conversion, we found 15% butyl undecanoate, 79% butyl 2-methyldecanoate, and 6% butyl 2-ethylnonanoate in the reaction products.

The reaction of an equimolar $CO—C_2H_4$ mixture at atmospheric pressure with a solution of 0.1 mmole $(PPh_3)_4Pd$, 0.2 mmole PPh_3, and 0.3 mmole PTSA in 10 ml ethyleneglycol at 60°C over 10 h led to 82 mmoles (2-ethoxyethyl) propionate, while a similar reaction in 10 ml 2-methoxyethanol using 0.4 mmole PPh_3 and 0.6 mmole PTSA over 5 h led to 110 mmoles (2-methoxyethyl) propionate.

LITERATURE CITED

1. A. D. Karpyuk, M. I. Terekhova, N. D. Kolosova, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 3, 639 (1985).
2. N. G. Mekhryakova, L. G. Bruk, O. L. Kaliya, et al., Kinet. Katal., 20, 629 (1979).

Institute of Structural Macrokinetics, Academy of Sciences of the USSR, Chernogolovka. L. Kossuth University, Debrecen, Hungary. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, p. 743, March, 1989. Original article submitted July 12, 1988.

0568-5230/89/3803- 0669$12.50