New Catalyst for the Synthesis of Dialkyl Ketones from Olefins, Carbon Monoxide, and Hydrogen

Vladimir N. Zudin,* Galina N. Il'inich, Vladimir A. Likholobov, and Yurii I. Yermakov
Institute of Catalysis, Novosibirsk 630090, U.S.S.R.

Dialkyl ketones are formed in mild conditions (30—70 °C, 1 atm) from H_2 + CO + C_2H_4 or C_3H_6 in aqueous trifluoroacetic acid solutions of a Pd^{II} triphenylphosphine complex.

During hydroformylation of olefins dialkyl ketones may be formed in small amounts. Attempts were made[1—3] to find reaction conditions favouring the predominant formation of dialkyl ketones from olefins, CO, and H_2 (or H_2O). During our previous study of the catalytic properties of palladium phosphine complexes it was found that contacting ethylene or propylene with a homogeneous catalyst for the water gas shift reaction (aqueous solution $CF_3CO_2H + Pd^{II} + PPh_3$)[4] resulted in the catalytic synthesis of C_5 or C_7 dialkyl ketones [reaction (1)].[5] The rate of ketone formation in this reaction was equal to the rate of CO_2 formation and was *ca.* 2 mol/g-atom Pd × h at 70 °C.

$$2C_nH_{2n} + 2CO + H_2O \xrightarrow[\substack{30\text{—}70\,^\circ C;\\ 1\text{ atm}\\ (n\,=\,2\text{ or }3)}]{Pd^{II},\ PPh_3} (C_nH_{2n+1})_2CO + CO_2 \quad (1)$$

$$2C_nH_{2n} + CO + H_2 \xrightarrow[\substack{30\text{—}70\,^\circ C;\\ 1\text{ atm}\\ (n\,=\,2\text{ or }3)}]{Pd^{II},\ PPh_3} (C_nH_{2n+1})_2CO \quad (2)$$

We report herein that C_5 or C_7 dialkyl ketones may be catalytically synthesised in aqueous trifluoroacetic acid solutions as in reaction (2). In the case of ethylene, reaction (2) proceeded with 95—99% selectivity (the by-products were propionic acid and traces of propionaldehyde) and with a high rate of diethyl ketone formation [up to 35 mol/g-atom Pd × h; Figure 1, curve (A)]. In the case of propylene the main reaction products were isomeric dipropyl ketones, and the by-products were butyric acids and small amounts of butyraldehydes and several unidentified products. For both olefins in the conditions of reaction (2) only traces of alkanes and CO_2 were formed.

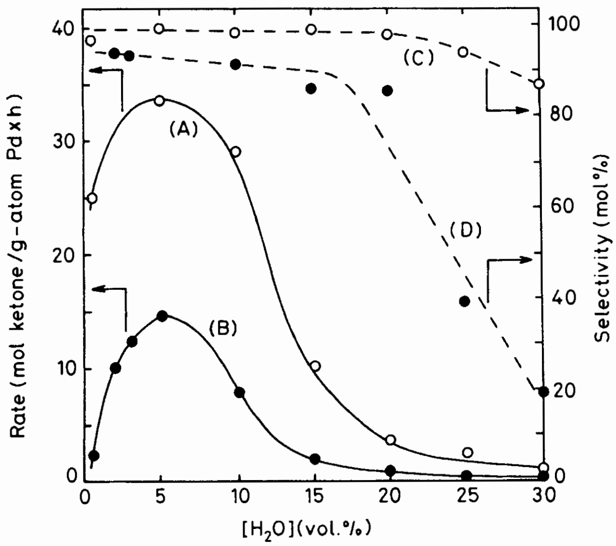

Figure 1. The dependence of the rate [curves (A) and (B)] and selectivity (relative to the sum of the ketones and acids) [curves (C) and (D)] of ketone formation upon the concentration of water in CF_3CO_2H (○ diethyl ketone; ● dipropyl ketones). {For all the runs: volume of solution 20 ml; [Pd] = 5 × 10^{-2} M; [PPh_3] = 0.5 M; the starting compound for palladium was $Pd(OAc)_2$; temperature 70 °C; gas mixture 'olefin : CO : H_2 2 : 1 : 1'}.

We have found that the rate and selectivity (relative to the sum of the ketones and acids formed) of ketone formation in reaction (2) depend on the concentration of water in CF_3CO_2H (Figure 1). Furthermore, the concentration of water also influences the distribution of isomers of dipropyl ketone. For example, at very low concentrations of water the molar ratio of 2,4-dimethylpentan-3-one:2-methylhexan-3-one:heptan-4-one in the product mixture was *ca.* 1 : 2 : 1 while at 25—30 vol. % water this ratio was *ca.* 1 : 5 : 1.

We believe that in both reactions (1) and (2), a hydride complex of palladium is formed and that the catalytic cycle involves olefin insertion into a Pd–H bond and CO insertion into a Pd–C bond. The difference between reactions (1) and (2) lies in the route to the palladium hydride complex. In reaction (1) the Pd–H bond is formed in the (rate-determining) reduction of Pd^{II} by CO followed by proton addition to the resulting Pd(0) species. In reaction (2) the Pd–H bond is probably formed by heterolytic rupture of hydrogen by the Pd^{II} complex.

$$\left.\begin{array}{l}(3a)\ L_2PdX_2 + CO + H_2O + L_2 \longrightarrow L_4Pd + CO_2 + 2HX\\[2ex] (3b)\ L_4Pd + HX \longrightarrow L_mPd(H)X\end{array}\right\}\ \text{Reaction (1)}$$

$$(4)\ L_2PdX_2 + H_2 \rightleftharpoons L_mPd(H)X + HX \qquad \text{Reaction (2)}$$

$$(5)\ L_mPd(H)X + C_nH_{2n} \rightleftharpoons L_mPd(C_nH_{2n+1})X$$

$$(6)\ L_mPd(C_nH_{2n+1})X + CO \rightleftharpoons L_mPd(COC_nH_{2n+1})X$$

$$(7)\ L_mPd(COC_nH_{2n+1})X + C_nH_{2n} + HX \longrightarrow L_2PdX_2 + (C_nH_{2n+1})_2CO$$

$$(8)\ L_mPd(COC_nH_{2n+1})X + H_2O \longrightarrow L_mPd(H)X + C_nH_{2n+1}CO_2H$$

Therefore, the catalytic formation of ketones from reactions (1) and (2) may be represented in the set of equations (3)—(7) (L = PPh_3, X = CF_3CO_2, n = 2 or 3, m = 2 or 3). By-products (carboxylic acids) were formed according to reaction (8).

Steps (7) and (8) appear to be competitive since the selectivity of ketone formation decreases with rising concentration of water [Figure 1, curves (C) and (D)].

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