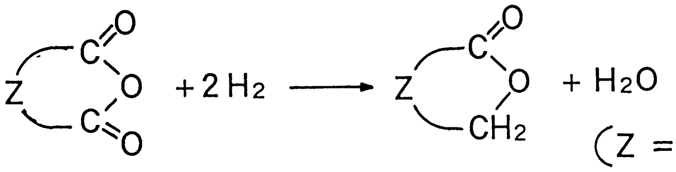
CHEMISTRY LETTERS, pp. 553-554, 1991

Hydrogenation Reaction of Carboxylic Anhydrides Catalyzed by a New and Highly Active Cationic Ruthenium Complex

Yoshinori HARA and Keisuke WADA*
Research Center, Mitsubishi Kasei Corporation,
1000 Kamoshida-cho, Midori-ku, Yokohama 227

A ruthenium complex prepared from tris(acetylacetonato)-ruthenium, triphenylphosphine, and a strong acid showed high activity and selectivity in hydrogenation reaction of carboxylic anhydride. The structure of the complex was assigned to be mer-$HRu(PR_3)_3(S)_2^+$, (S: solvent), which is more active than the neutral ruthenium complexes.

Catalytic hydrogenation of carboxylic anhydride to the corresponding ester or lactone has been studied for $RuCl_2(PPh_3)_3$,1) $Ru_2Cl_4(dppb)_3$,2) and $H_4Ru_4(CO)_8(P^nBu_3)_4$3) catalyst systems. The catalytic activity in all of those works, however, was not enough for the reaction to exceed over 50% conversion, even for a long reaction period.


(1)

$(Z = 2CH_3, -(CH_2)_2-, -C_6H_4-)$

During a course of study on hydrogenation of carboxylic anhydride catalyzed by ruthenium complex, we found that the rate of hydrogenation was accelerated remarkably by addition of a strong acid to the catalytic system. The strong acid improved strikingly also the selectivity for the corresponding ester or lactone. The effect of the added strong acid is illustrated in Table 1. The new catalyst system attained much higher activity and selectivity than those of not only the catalysts cited above1-3) but also the conventional copper-chromium mixed oxide.4)

Other strong acids like benzenesulfonic acid, methanesulfonic acid, ammonium tetrafluoroborate, and ammonium hexafluorophosphate exhibited the similar effect to p-toluenesulfonic acid. It was noted that the hydrogenation of 3-hydroxyphthalic anhydride afforded a substituted phthalide in which the sterically less hindered carbonyl group was exclusively hydrogenated, thus, giving 7-hydroxy- and 4-hydroxyphthalide in 60.0 and

Table 1. Effect of p-Toluenesulfonic Acid in Catalytic Hydrogenation of Carboxylic Anhydrides by Ruthenium Catalysts[a)]

Catalyst	Carboxylic anhydride	Product	Activity[b)]	Select.[c)]
$H_4Ru_4(CO)_8(P^nBu_3)_4$	Acetic anhydride	Ethyl acetate	68	100
$Ru(acac)_3/P(^nC_8H_{17})_3$/p-TsOH	〃	〃	200	99
$RuCl_2(PPh_3)_3$	Succinic anhydride	γ-Butyrolactone	5	99
$Ru(acac)_3/P(^nC_8H_{17})_3$	〃	〃	120	50
$Ru(acac)_3/P(^nC_8H_{17})_3$/p-TsOH	〃	〃	257	95
$Ru(acac)_3/P(^nC_8H_{17})_3$/p-TsOH	Phthalic anhydride	Phthalide	164	85

a) Tris(acetylacetonato)ruthenium 0.05 mmol, tri-n-octylphosphine 0.5 mmol, p-toluenesulfonic acid 0.4 mmol, carboxylic anhydride 40 mmol, tetraglyme 16 ml, hydrogen 3 MPa, 200 °C, 2 h.

b) mol product/g-atom Ru.h.

c) Selectivity for product in mol%.

0.0% yield, respectively. The analogous regioselectivities were reported for 2-methylsuccinic anhydride[2)] and 2,2-dimethylsuccinic anhydride.[5)]

The ^1H and ^{31}P NMR studies at room temperature[6)] suggested that a cationic complex, mer-$HRu[P(^nC_8H_{17})_3]_3(S)_2{}^+$, (S: solvent), $\underset{\sim}{1}$, was formed in the catalyst solution. As compared with the neutral complex, the complex $\underset{\sim}{1}$ was believed to interact more effectively with carbonyl moiety of the anhydrides, thus, leading the higher catalytic activity.

Typical procedure: In an autoclave with a magnetic stirrer, $Ru(acac)_3$ (0.05 mmol), tri-n-octylphosphine(0.5 mmol), succinic anhydride(40 mmol), and tetraglyme(16 ml) were placed. The reaction was carried out under hydrogen 3 MPa at 200 °C for 2 h. The conversion of succinic anhydride was 60% and selectivity for γ-butyrolactone was 95%.

References

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6) ^1H NMR of $\underset{\sim}{1}$ in glyme shows a doublet-triplet at -6.7 ppm assignable to Ru-H coupled with two magnetically equivalent phosphorus nuclei ($J(H\text{-}P_{cis})$ = 25 Hz) and one phosphorus nuclei which is trans to a hydride ($J(H\text{-}P_{trans})$ = 114 Hz). $^{31}P\{^1H\}$ NMR of $\underset{\sim}{1}$ in tetraglyme is in full agreement with this structure, two phosphorus nuclei giving rise to a doublet at 18.8 ppm and one phosphorus nuclei giving a triplet at -0.4 ppm ($J(P_{cis}\text{-}P_{trans})$ = 20 Hz).

(Received October 30, 1990)