Hydrogenating Activity of an Iridium Catalyst

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COLLOIDAL iridium possesses high activity as a catalyst for hydrogenation of aromatic nitro-compounds, especially in alkaline medium.[1] The activity of an iridium catalyst prepared by Adams' method has not previously been reported in this context. The author now reports that such a catalyst is useful for reducing aromatic nitro-compounds to hydroxylamines.

The Table shows results obtained on hydrogenation of a number of aromatic nitro-compounds, carried out with the iridium catalyst prepared according to a modified Adams' method; 80% aqueous ethanol (30 ml.) was the solvent, except where otherwise stated, and the hydrogenations were effected at atmospheric pressure and 25°. The reaction was stopped when about 2 mol. of hydrogen had been absorbed. The hydroxylamines produced were identified by their melting points[2,3] and their infrared spectra, which showed bands[4] at 3200—3280 (ν_{NH}) and 914—938 (ν_{NO}) cm.$^{-1}$

N-Phenylhydroxylamine is known[2] to be produced when nitrobenzene is hydrogenated with palladium–charcoal as catalyst. However, when platinum or palladium catalysts prepared by Adams' method were used, the hydrogenation gave mainly aniline (even when the reaction was stopped after 2 mol. of hydrogen had been consumed) and no *N*-phenylhydroxylamine could be isolated. During hydrogenation with an iridium catalyst, however, the rate of consumption of hydrogen decreased rapidly after 2 mol. of hydrogen had been absorbed; with the other catalysts no such decrease was observed. Presumably, therefore, the relatively slow rate of hydrogenation of the hydroxylamines with an iridium catalyst is the factor which

TABLE

Reactant	Reactant Conc. (mM)	Wt. of oxide (mg.)	Reaction time (min.)	Hydroxylamine yield (%)[a]	Hydroxylamine m.p. (°c)[b]
Nitrobenzene	30	50	60[c]	58[d]	81[2]
o-Nitrotoluene	20	30	280	20	44[3]
m-Nitrotoluene	20	30	90	77	68[3]
p-Nitrotoluene	20	30	110	75	98[3]
o-Chloronitrobenzene	20	30	67	25	56[3]
m-Chloronitrobenzene	10	30	43	73	49[3]
p-Chloronitrobenzene	20	50	49	83	86[3]
p-Bromonitrobenzene	20	30	130	65	90[3]
p-Nitroanisole	20	30	180	36[d]	98[3]
1-Nitronaphthalene	10	30	76	69	79[3]
2,4-Dinitrotoluene	10	30	88	90[e]	100[2]

[a] As the product was unstable and partially decomposed during recrystallization, yield of crude product (m.p. is 2—8° lower than authentic sample) is shown.
[b] M.p. of pure sample obtained by recrystallization.
[c] Solvent, ethanol.
[d] Yield of pure product.
[e] Yield of 4-hydroxylamino-2-nitrotoluene.

permits their isolation under these conditions. Prolonged hydrogenation did, however, produce the corresponding anilines in 70—90% yields.

The iridium catalyst was ineffective for hydrogenation of cyclohexene, allyl alcohol, styrene, cyclohexanone, acetophenone, mesityl oxide, acetonitrile, and acetoxime under the same conditions.

An iridium–platinum catalyst, prepared by a modification of Adams' method[5] [70% iridium by weight] was found to hydrogenate nitrobenzene to *N*-phenylhydroxylamine at a rate 2—3 times faster than the iridium catalyst, but the yield was lower (*ca.* 40%).

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