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THE RUTHENIUM CARBONYL CATALYZED REDUCTION OF NITRO COMPOUNDS BY PHASE TRANSFER CATALYSIS

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Summary: Amines were obtained in excellent yields by treatment of nitro compounds, at room temperature and atmospheric pressure, with carbon monoxide, ruthenium carbonyl as the metal catalyst, and benzyltriethylammonium chloride as the phase transfer catalyst in an aqueous base-organic solvent system.

In 1977, one of us described the application of phase transfer catalysis to the stoichiometric reduction of nitro compounds to anilines by triiron dodecacarbonyl in a nitrogen atmosphere[2]. It was later observed that the yields of aromatic amines were substantially lower when the deoxygenation was effected in an atmosphere of carbon monoxide[3]. We now wish to report that ruthenium carbonyl can catalyze the reduction of nitro compounds at room temperature and atmospheric pressure . Furthermore, as far as reactivity in a carbon monoxide or nitrogen atmosphere is concerned, the behavior of triruthenium dodecacarbonyl is the reverse of that of triiron dodecacarbonyl.

Reaction of a nitroarene (1) with a catalytic quantity of ruthenium carbonyl, benzyltriethylammonium chloride as the phase transfer catalyst, sodium hydroxide (5N), benzene containing

$$\underset{\underline{1}}{RNO_2} \xrightarrow[\substack{CH_3OCH_2CH_2OH, PhCH_2N(C_2H_5)_3{}^+Cl^- \\ \text{r.t., 1 atm.}}]{CO, Ru_3(CO)_{12}, 5N\ NaOH, C_6H_6} \underset{\underline{2}}{RNH_2}$$

a small amount of 2-methoxyethanol, and carbon monoxide, at room temperature and atmospheric pressure, affords the corresponding aniline (2)[4]. The reaction times and product yields are listed in Table I.

The purpose of the phase transfer catalyst is to accelerate the rate at which the presumed benzyltriethylammonium carbonylruthenate cluster intermediate, $[PhCH_2N(C_2H_5)_3][HRu_3(CO)_{11}]$, is formed, with 2-methoxyethanol increasing the solubility of this anionic cluster in the organic phase. The presence of other cluster anions in aqueous base/organic solution, such as $Ru_6(CO)_{18}{}^{-2}$, $HRu_6(CO)_{18}{}^{-}$, and $H_3Ru_4(CO)_{12}{}^{-}$, is also conceivable[5,6]. Reaction will occur in the absence of 2-methoxyethanol but at the expense of both reaction rate and product yields. Note that the concentration of sodium hydroxide (5N) used is important, since anilines were formed in lower yields at either lower or higher base concentrations.

Aromatic amines are formed in about five times greater yield using a carbon monoxide rather than a nitrogen atmosphere. This reversal in behavior, when compared with the stoichiometric reduction of nitro compounds by $Fe_3(CO)_{12}$, is intriguing, and is suggestive of the participation of different species in the reactions of the iron and ruthenium hydride intermediates with nitro compounds.

TABLE I
Yields of Amines[a]

Nitro compound	Reaction time (hr)	Product	Yield (%)
Nitrobenzene	9.0	Aniline	100
p-Nitrotoluene	8.0	p-Toluidine	94
p-Nitroanisole	7.0	p-Anisidine	84
p-Chloronitrobenzene	3.0	p-Chloroaniline	100
p-Nitrobenzophenone	4.5	p-Aminobenzophenone	100
2,6-Dimethylnitrobenzene	25	2,6-Dimethylaniline	8
2-Nitrofluorene	20	2-Fluorenylamine	95
1-Nitropropane	17	n-Propylamine	85

[a] Amines were identified by comparison of physical properties with those for authentic materials.

Examination of Table I indicates that the yields of amines (2) are excellent, with the exception of the hindered nitro compound, 2,6-dimethylnitrobenzene. The presence of electron-withdrawing groups (e.g., chloro, carbonyl--note that the latter is unaffected) increases the rate of reduction of 1. This method is significantly milder than that using water gas shift reaction conditions [100°C, 500 psi pressure][7]. Since the ruthenium carbonyl catalyzed phase transfer process occurs at one atmosphere pressure, it is also less drastic than when iron pentacarbonyl was employed as the catalyst for the nitro reduction by carbon monoxide and water [1700 psi pressure][7].

The following general procedure was used: to $Ru_3(CO)_{12}$ (0.03 mmol) in benzene (20 ml) containing 2-methoxyethanol (5 ml) was added benzyltriethylammonium chloride (0.25 mmol) in 5N NaOH (10 ml). The reaction mixture was stirred for one hour under an atmosphere of carbon monoxide. The nitro compound (5.0 mmol) in benzene (5 ml) was added and stirring was continued until the reaction was complete (followed by thin-layer chromatography). The organic layer was separated, the aqueous layer was acidified to pH 6 with dilute HCl, and the amine was extracted with ether, and the ether extract was dried ($MgSO_4$). Amine (2) was obtained on evaporation of the solvent and further purified, if necessary, by thin-layer chromatography on silica gel using hexane/ethyl acetate.

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References

1. E.W.R. Steacie Fellow, 1980-82.
2. H. des Abbayes and H. Alper, J. Am. Chem. Soc., 99, 98 (1977).
3. H. Alper and H.N. Paik, Nouv. J. Chim., 2, 245 (1978).
4. The reduction of organic substrates by CO and water has also been observed by G. Gelbard (Tenth Sheffield International Symposium on Organometallic and Inorganic Chemistry, July 1979).
5. C. Ungermann, V. Landis, S.A. Moya, H. Cohen, H. Walker, R.G. Pearson, R.G. Rinker and P.C. Ford, J. Am. Chem. Soc., 101, 5922 (1979).
6. P.F. Jackson, B.F. Johnson, J. Lewis, M. McPartlin and W.J.H. Nelson, J. Chem. Soc., Chem. Commun., 735 (1979).
7. K. Cann, T. Cole, W. Slegeir, and R. Pettit, J. Am. Chem. Soc., 100, 3969 (1978).

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