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CATALYTIC REDUCTIONS WITH FORMATE ION UNDER PHASE TRANSFER CONDITIONS

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Abstract: Formate ion was extracted as ion pair into organic solvents and catalytically reduced chalcone in presence of homogeneous ruthenium phosphine complex.

Formic acid is a very convenient hydrogen donor and was applied for the reduction of numerous substrates such as olefins[1], aromatic nitro compounds[2] and aryl halides[2].

Several authors have observed that formic acid salts are far more active hydrogen donors than formic acid itself both in catalytic[3] and non-catalytic[4] systems. We have found that formic acid rapidly decomposes to hydrogen and carbon dioxide in the presence of transition metals; therefore the yields in transfer hydrogenation with formic acid are relatively low unless large excesses of the acid are applied. Practically no competitive decomposition occurs in reductions with formate ion.

The formate salts suffer, however, from a major disadvantage in being unsoluble in common organic solvents and require the presence of polar solvents e.g. DMF or DMSO which complicate the process and the separation of the products.

We have now found that formate ion can be extracted from aqueous phase into organic phase by means of lipophilic quaternary ammonium or phosphonium salts. This observation allows us to apply aqueous solutions of sodium formate for reduction of substrates in the organic phase in the presence of catalytic amounts of quaternary salts. This method adds to the very few existing reduction methods suitable for phase transfer catalysis[5].

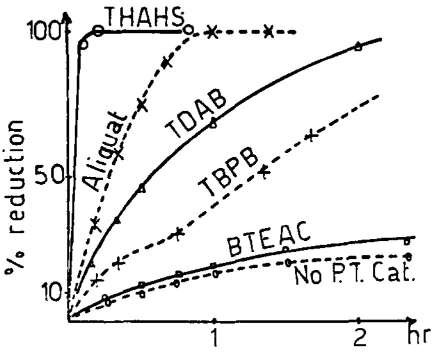
The new method is demonstrated by the selective formate reduction of 1,3-diphenyl-1-propene-3-on (chalcone) to 1,3-diphenylpropane-3-on in the presence of $RuCl_2[PPh_3]_3$ and quaternary salts (eq.1).

$$(1)\ H_2O(\ell) + 2C_6H_5CH{=}CHCOC_6H_5(org) + 2HCOONa(aq) \longrightarrow 2C_6H_5CH_2CH_2COC_6H_5(org) + CO_2(g) + Na_2CO_3(aq)$$

In a typical example, 19 ml of degassed ortho-dichlorobenzene (solvent), 1 ml of diphenylmethane (internal standard), 1.0413 g chalcone (5×10^{-3} mole) and 50 mg $RuCl_2\ (PPh_3)_3$ (5.2×10^{-5} mole) are gently warmed until a clear orange-brown solution is obtained. A solution of 3.4 g sodium formate and (1.04×10^{-4} mole) of tetrahexylammonium hydrogensulfate in 20 ml water is added. The mixture is stirred by a magnetic stirrer at a constant rate and warmed in an oil bath to reflux temperature (382K) for 10 minutes. GLC analysis of the organic phase showed 99% conversion with 100% selectivity to 1,3-di-phenylpropane-3-on. During the reaction carbon dioxide is evolved from the system and sodium carbonate is found in the aqueous phase.

The effect of other ammonium and phosphonium salts on the system as well as the progress of the reaction in the absence of phase transfer catalysts is shown in the figure.

The Effect of Phase Transfer Catalysts Reaction (1)



THAHS-tetrahexylammoniumhydrogensulphate
Aliquat 336: tricaprylylmethylammonium chloride
TDAB: tetradecylammonium bromide
TBPB: tetrabutylphosphonium bromide
BTEAC: benzyltriethylammoniumchloride
Temperature: 382K

Molar Ratio:	Ru.Cat.:	PT Cat.:	Substrate:	Formate
	1	2	100	1000

In a similar manner we have quantitatively reduced C=C bonds in other α,β unsaturated carbonyl compounds typically: benzal acetone, ethyl cinnamate and ring substituted chalcones. The phase transfer catalytic effect was also clearly demonstrated in reductions of nitroaromatics and hydrogenolysis of aryl halides.

Other metal complexes have been successfully applied in the two-phase formate reduction systems, e.g., $RhCl(PPh_3)_3$ $PdCl_2(PPh_3)_2$ and $Pd(PPh_3)_4$.[6]

We suggest that the active species in these systems is the extracted formate ion which adds to the metal catalyst by ligand exchange and then decomposes to metal hydride and CO_2. The hydride complex reacts with the acceptor in a mechanism common in catalytic hydrogenation.

Detailed mechanistic studies of the system and its synthetic applications are now underway.

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