Investigation of the Wacker Process in Formamide Microemulsions¹

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Formamide microemulsions have been used as reaction media for the Wacker process, giving much faster oxidation of hex-1-ene to hexan-2-one than in classical media.

The Wacker process for the catalytic oxidation of alkenes is an important industrial process which has been in widespread use for the last 20 years.² It involves the transformation of a terminal olefin, RCH=CH₂, into a ketone, RCOMe, by water using a palladium(π) salt as catalyst, equation (1). Pd^{II} is then regenerated either with Cu^{II}/O₂, equations (2) and (3), or a quinone, equation (4).

$$RCH=CH_2 + Pd^{II} + H_2O \rightarrow RCOMe + Pd^0 + 2H^+ (1)$$

$$Pd^{0} + 2Cu^{II} \rightarrow 2Cu^{I} + Pd^{II}$$
(2)

$$2H^+ + 1/2 O_2 + 2Cu^I \rightarrow 2Cu^{II} + H_2O$$
 (3)

$$Pd^{0} + 2H^{+} + 0 = 0 \rightarrow Pd^{11} + H0 \longrightarrow OH$$
 (4)

The reaction was studied in both homogeneous and heterogeneous phases. Homogeneous conditions require the use of complexes such as Na_2PdCl_4 , $PdCl_2(PhCN)_2$, $PdCl_2(MeCN)_2$ etc.³ since $PdCl_2$, the least expensive salt, is almost insoluble in organic solvents and is only slightly soluble in water (0.7 g l⁻¹). For heterogeneous conditions, biphasic media composed of mixtures of dimethylformamide (DMF), water, and palladium chloride have been employed. These less costly systems give good yields, although the reactions are generally slow.² Formamide is a good solvent for salts with large ions.⁴ We found the solubility of palladium chloride in formamide to be 50 g l⁻¹, and therefore decided to employ it in the Wacker process.

In previous studies we showed that it was possible to prepare homogeneous monophasic microemulsions with hydrocarbons and formamide, which are normally immiscible, by the addition of a surfactant and cosurfactant.^{4,5} We investigated the Wacker process in (i) biphasic media, replacing the usual dimethylformamide by formamide, and (ii) homogeneous media using a standard formamide microemulsion. Such media have been used in this laboratory for the study of various reactions (photoamidation,⁶ Diels–Alder reactions,⁷ polymerization⁸ *etc.*).

We report here results obtained for hex-1-ene using palladium chloride, with benzoquinone to regenerate Pd^{II}.

 Table 1. Effect of the medium on the oxidation of hex-1-ene by the Wacker process.

Medium	Induction period/min	Rate constant/ 10 ³ Kg mol ⁻¹ s ⁻¹	Reaction time/ min ^a
DMF-H ₂ O	100—110	9.6	~280
$HCONH_2 - H_2O$	>12 h		
Microemulsion M	0	13.4	120
Microemulsion N	0	29.5	80

^a All reactions went to completion leading to a single ketone, hexan-2-one (from n.m.r. and g.c. data).

The microemulsion system consisted of formamide, hex-1ene, propan-2-ol as cosurfactant, and C_9H_{19} - C_6H_{4} -(OCH₂)₈OH as surfactant. The formamide : surfactant ratio (w/w) was fixed at 2:1. Water was then added in a molecular



Figure 1. Phase diagram of the Wacker catalytic microemulsion system $HCONH_2-C_9H_{19}C_6H_4(OCH_2CH_2)_8OH$ (2:1 w/w)-propan-2-ol-hex-1-ene-water (1.56:1 w/w).



Figure 2. Kinetics of Wacker oxidation of hex-1-ene in DMF-H₂O (\bigcirc), HCONH₂-H₂O (+), and microemulsions M (\triangle) and N (×).

ratio of 3:1 with hex-1-ene under the usual conditions² giving a hex-1-ene : water ratio of 1.56:1 (w/w). The pseudoternary phase diagram⁵ is shown in Figure 1. Benzoquinone and palladium chloride were then introduced into the microemulsions (M and N) at the start of the reaction, to give an equimolar hex-1-ene : benzoquinone ratio and a hex-1-ene : PdCl₂ molar ratio of 100:1. In order to compare our results with other published studies we investigated the oxidation of hex-1-ene in the heterogeneous medium, water-DMF.⁴

The reaction kinetics were studied by periodic gas chromatographic analysis for hex-1-ene in gas samples from a completely closed reactor. The results obtained in DMF- H_2O , $HCONH_2-H_2O$, and in microemulsions M and N are shown in Figure 2 and Table 1. (i) The reaction carried out in DMF-water started after an induction period of around 100 min, this delay can be attributed to poor contact between the reactants and the catalyst. (ii) No reaction could be detected in the HCONH₂ water mixture, owing either to poor contact with the catalyst or strong complexation of palladium by formamide (by either nitrogen or oxygen co-ordination⁹). The existence of such a complex was detected by u.v. spectroscopy. (iii) In the microemulsions (M and N) the main feature was the absence of an induction period. In such homogeneous media there is good contact between reactants and catalyst, and the reaction starts immediately. It should also be noted that the overall reaction was faster than in the water-DMF mixture, particularly in the olefin-rich microemulsion N, which gives three-fold increase in reaction velocity with respect to the classical medium.

This preliminary study provides the first demonstration of the use of formamide microemulsions as reaction media for the Wacker process. This approach shows considerable promise owing to the absence of an induction period and an increase in overall reaction rate.

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