Homogeneity of Olefin Metathesis Reactions Catalysed by Co-ordination Complexes

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Summary Some, and perhaps all, WCl_6-based co-ordination catalysts for olefin metathesis are insoluble in the reaction medium and should be considered as heterogeneous catalysts.

OLEFIN metathesis has been much studied[1] since the original report by Banks and Bailey.[2] We have investigated the mechanism for the class of catalysts described[1] as yielding homogeneous systems and have found that at least for the co-ordination catalysts derived from WCl_6 the primary catalytic activity appears to reside in an insoluble fraction.

Activation of WCl_6 in a benzene reaction medium by alkylating reagents, following basic literature procedures, yields reaction systems with a reactivity order in the metathesis reaction of (WCl_6–EtOH–4EtAlCl$_2$)[3] > (WCl_6–2EtAlCl$_2$)† > (WCl_6–2Bu^{n}Li)[4] > (WCl_6–R$_2$Zn).[5] In all these systems evidence was obtained for the presence of solids, in particular for the alkyl-lithium system. Following the Wang–Menapace[4] procedure, the metathesis reaction system of C_6H_6, *cis*-pent-2-ene, Bu^{n}Li, and WCl_6, was filtered. The colourless filtrate contained less than 10 p.p.m. tungsten and yielded no metathesis products. In contrast the solids, which contained Li, W, Cl, C, and H, after addition to a standard C_6H_6–*cis*-pent-2-ene metathesis solution showed a catalytic activity nearly as high as the standard, unfiltered reaction system. This indicates clearly that the WCl_6–Bu^{n}Li reagent is a *heterogeneous* catalyst. Similar results were obtained with the Me$_2$Zn system. Filtration yielded a solid which was catalytically active although with only about one-sixth of the activity of an unfiltered reaction mixture. In this system, the filtrate was coloured and contained >100 p.p.m. tungsten. Metathesis occurred in the filtrate at a rate comparable to the standard zinc catalyst mixture but solids continued to form

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† We find that alcohol is not essential to high reactivity in the aluminum system. If the Calderon *et al.*[3] procedure is employed with exclusion of alcohol and with a W : Al ratio of 1 : 2, equilibrium in the metathesis reaction is attained in *ca.* 35 min compared with *ca.* 3 min in the analogous ethanol-modified[3] system.

throughout the period required for equilibrium to be attained. We suggest from these results that the rate of catalyst formation in this zinc system is low and that the actual catalyst is heterogeneous. In any case, the experiments clearly establish that a solid phase, active as a catalyst in the metathesis reaction, is produced in the dialkylzinc system. Treatment of WCl_6 with 1 equiv. of EtOH prior to the addition of dialkylzinc raises the activity of this metathesis system about ten-fold. In this modified system, solids separate throughout the *ca.* 2 h period required for attainment of metathesis equilibrium and the solution changes from red to yellow-brown.

We believe that the two aluminium-based systems *may* be heterogeneous, although we cannot be certain because of experimental difficulties [high reactivity and low tungsten concentration‡ (*ca.* 100 p.p.m.)]. A solid phase was evident in the WCl_6–$2EtAlCl_2$ system, and filtration yielded a filtrate with $\leqslant$ 10 p.p.m. of tungsten and a solid, which was so fine that it penetrated the pores (4—5·5 nm) of the glass filter frit. After crushing or grinding the frit, low catalytic activity was observed, a result that may reflect inaccessibility of the solid surface to the metathesis solution or destruction of the catalyst by the grinding process. In the most active, alcohol-modified system, solids were visible (laser light beam) only after 5—10 min whereas metathesis equilibrium required only 2—3 min. Filtration gave similar results to the system without alcohol. In these experiments, the possibility that the catalyst reacted with the surface of the glass frit cannot be excluded, despite extensive precautions that included pretreatment of the filters with $EtAlCl_2$.

These co-ordination catalysts show individual variability in activity for olefin metathesis,[1] despite rigid attention to experimental detail; this is not inconsistent with a heterogeneous system.

Many heterogeneous catalysts[1] and some presumed homogeneous catalysts[1,6] are reported to be active for metathesis of terminal olefins. Not only are the above described catalysts derived from tungsten hexachloride essentially inactive for terminal olefins but their catalysis of internal olefin metathesis is strongly inhibited by the presence of terminal olefins, which demonstrates that metathesis catalysts are not of one specific stereochemical class. Also, the reactivities of these catalysts derived from tungsten hexachloride vary widely (unlike the formally analogous co-ordination catalysts[7] for olefin polymerization); times for metathesis equilibrium to be achieved range from minutes to days. We suggest that the second metal (Al, Zn, Li) centre as well as the tungsten, is intimately involved in the olefin metathesis reaction.

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‡ At higher concentrations of reagents, alkylation of benzene becomes the dominant reaction.

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