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The oligomerisation of ethene with catalysts exhibiting enzyme-like activities

Steven J. Brown and Anthony F. Masters *
Department of Inorganic Chemistry, University of Sydney, N.S.W., 2006 (Australia)

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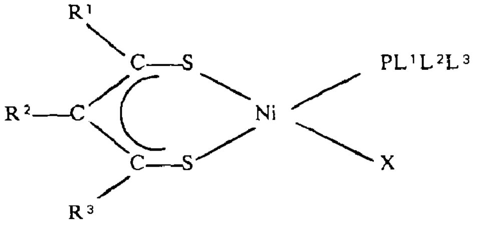
Abstract

The catalytic oligomerisation of ethene at about room temperature and one atmosphere of ethene by a series of catalysts derived from Ni(sacsac)PR_3Cl (sacsac$^-$ = $C_5H_7S_2^-$ = pentane-2,4-dithionate anion) is described. The catalytic activities and selectivities are shown to be dependent on the phosphine ligand and the reaction temperature. Activities of the order of 4×10^6 mol of ethene converted per mol of nickel per h (> 1000 s^{-1}) are reported. The catalysts are quite long-lived, more than 2×10^7 g of products can be produced per mol of nickel.

Introduction

Olefin oligomerisation is a pivotal process in the catalytic production of fuels and specialty chemicals. A number of very active olefin oligomerisation catalysts can be generated by combining a nickel compound with an alkylating or hydridic co-catalyst [1–4]. Catalysts of this type have been extensively investigated and several processes have been commercialized [5,6].

Air stable sixteen electron nickel complexes of the general formula Ni(R^2-R^1sacR^3sac)X($PL^1L^2L^3$), (R^j, L^j = alkyl or aryl; X = halide; sacsac$^-$ = $C_5H_7S_2^-$ = dithioacetylacetonate anion = pentane-2,4-dithionate anion) (I) when activated by a co-catalyst under mild conditions form extremely active olefin oligomerisation and isomerisation catalysts [7–10].



(I)

We have investigated the reaction rates and product distributions of a series of reactions between ethene and catalysts derived from (I; $R^1 = R^3 = CH_3$, $R^2 = H$, $X = Cl$) but with differing phosphine ligands. In the present series of experiments we have established that the previously reported activity [8] of these catalysts in their reactions with ethene were apparently determined by the reaction conditions. The earlier experiments were performed using a flow through system at less than complete conversion, and with activities determined by gas chromatographic analyses of the reaction products as a function of time. The turnover numbers determined in this manner significantly underestimated the true values of the turnover numbers, but were nevertheless useful in demonstrating that the compounds I formed highly active catalysts.

We have shown recently that the actual turnover numbers for propene oligomerization are almost two orders of magnitude higher than originally reported [9]. The present results demonstrate that the activities for ethene oligomerization are almost three orders of magnitude higher than originally reported. The experiments for determining such high activities at 100% conversions were performed as follows.

Experimental

The apparatus consisted of a 250 ml glass three-necked, flanged, Quickfit reactor vessel. One neck was fitted with a septum. One neck was connected to a vacuum/argon manifold. The central neck contained a dip tube connected via a calibrated flow meter and pressure regulator to an ethene cylinder. The temperature of the solution was monitored via a thermocouple. Ethene was introduced below the surface of the vigorously stirred liquid. The glass apparatus was assembled hot (90 °C) and was then repeatedly evacuated and filled with ethene. The reactor was then charged with 30 ± 0.5 ml of dried, distilled, degassed chlorobenzene and Et_2AlCl (0.2 ± 0.05 ml, 1.7 ± 0.4 mmol) under an atmosphere of ethene (24 mmHg above atmospheric). The apparatus was conditioned by stirring for 1 h at ambient temperature. The vigorously stirred mixture was then treated with a solution of the nickel precursor I in chlorobenzene (3.5×10^{-4} *M*) in 10×1 ml aliquots and the rate of ethene uptake was measured using the flow meter. After all ten aliquots of catalyst were added and the ethene consumption had fallen to zero, 10 ml of water was added. The weight and volume of the products were recorded and the product distribution was determined by gas chromatography.

Discussion

No reaction was observed in solutions of the nickel complex alone, nor of the alkyaluminium co-catalyst alone under these conditions. Because of the exothermic nature of the oligomerisation reaction and the very high activities, the reaction temperature proved difficult to control. The activites of a large number of catalysts over a range of temperatures are illustrated in Table 1. The stirring speed was high enough that the reaction rate was independent of stirring speed. All the catalysts tested showed extremely high activites, with turnover numbers (moles of ethene converted per mole of catalyst per second) in excess of 1000 s^{-1} at or just above ambient temperature. These catalysts are thus some of the most active, if not the most active, olefin oligomerisation catalysts reported. Turnover numbers as high as

Table 1

Variation in catalytic activity with phosphine

Catalyst precursor Ni(sacsac)PR$_3$Cl PR$_3$ =	Temperature (°C)	Activity		Mass of products per mol of nickel (kg)
		hr^{-1}	s^{-1}	
PBu$_3$	35	5.8×10^6	1600	3900
PBu$_3$	0	3.0×10^6	800	9300
PBu$_3$	−20	2.3×10^6	600	21700
P(C$_8$H$_{17}$)$_3$	32	4.6×10^6	1300	4500
P(C$_8$H$_{17}$)$_3$	0	2.7×10^6	750	5600
PEt$_3$	27	4.6×10^6	1300	2200
P(C$_{16}$H$_{33}$)$_3$	32	4.1×10^6	1100	3200

230 s^{-1} at −55°C have been reported for the catalytic oligomerisation of propene using the catalyst system Ni(η^3-C$_3$H$_5$)Br[P(C$_6$H$_{11}$)$_3$]/EtAlCl$_2$/C$_6$H$_5$Cl [12], but the activity of this system at higher temperatures has not been reported. By comparison, the turnover numbers for most enzymes with their physiological substrates are in the range 0.2 to 10^5 s^{-1} [13,14] with very fast enzymic reactions (e.g., carbonic anhydrase) having turnover numbers of ca. 1000000 s^{-1} [14]. The observed activities of catalysts derived from I do not appear to be very dependent on the nature of the trialkylphosphine ligands used in this study. However, we have noted previously that the phosphine is presumably bound to the complex at least during some point of the catalytic cycle, since different phosphines show marked product directing effects in the oligomerization of propene [7,8]. Reducing the reaction temperature results in a reduction in activity, as expected, but also results in a greater product yield, possibly demonstrating a degree of thermal instability associated with the catalyst.

The products of the ethene oligomerisation reaction are dependent on the reaction temperature (Table 2). Reducing the reaction temperature gives fewer higher oligomers in both cases examined. This is particularly so in the case of the catalyst derived from Ni(sacsac)P(C$_8$H$_{17}$)$_3$Cl/Et$_2$AlCl. No correlation between the bulk of the phosphine substituent and the product distribution is apparent, although only a limited number of phosphine ligands has been surveyed. All isomers expected

Table 2

Variation in oligomeric products as a function of phosphine

Catalyst precursor Ni(sacsac)PR$_3$Cl PR$_3$ =	Temperature (°C)	Products (wt %)				
		C$_4$	C$_6$	C$_8$	C$_{10}$	C$_{12^+}$
PBu$_3$	35	43.0	51.5	4.5	0.6	0.4
PBu$_3$	0	54.4	43.4	2.1	0.1	–
PBu$_3$	−20	58.3	37.3	4.4	–	–
P(C$_8$H$_{17}$)$_3$	32	43.6	50.8	4.7	0.7	0.2
P(C$_8$H$_{17}$)$_3$	0	75.9	24.1	–	–	–
PEt$_3$	27	53.5	42.9	3.6	–	–
P(C$_{16}$H$_{33}$)$_3$	32	51.0	43.9	3.6	–	–

Table 3

Equilibrium butene isomer distribution as a function of phosphine

Catalyst precursor Ni(sacsac)PR_3Cl PR_3 =	Temperature (°C)	Isomer (%)		
		1-Butene	*trans*-2-Butene	*cis*-2-Butene
PBu_3	35	2	67	31
PBu_3	0	2	70	28
PBu_3	−20	4	69	27
$P(C_8H_{17})_3$	32	2	66	32
$P(C_8H_{17})_3$	0	2	61	37
$P(C_{16}H_{33})_3$	33	2	69	29
Thermodynamic:	27	2.5	73.8	23.8

from a catalytic cycle involving ethene substrate and nickel-hydride/nickel-alkyl intermediates are observed, as is illustrated by the butenes produced (Table 3). Within each oligomer fraction the distribution of isomers is close to the thermodynamic equilibrium isomer distribution. Although the deviations from the thermodynamic equilibrium distribution are small, the proportion of *cis*-2-butene is consistently high, and the proportion of *trans*-2-butene is consistently low. We have observed a similar effect on the equilibrium isomer distribution during 1-hexene isomerization [15]. The effect is probably steric in origin and may be consistent with a bimetallic nickel-aluminium intermediate.

The rates of olefin isomerisation by these catalysts are known to be considerably faster than the rate of oligomerisation [9]. To our knowledge the systems described here are amongst the most active synthetic homogeneous catalysts reported to date.

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References

1 G. Lefebre and Y. Chauvin, in R. Ugo (Ed.), Aspects of Homogeneous Catalysis, Ch. 3, 1970 p. 107.
2 P.W. Jolly and G. Wilke, The Organic Chemistry of Nickel, Vol. 2., Academic Press, New York, 1975.
3 B. Bogdanović, Adv. Organomet. Chem., 17 (1979) 105.
4 G. Henrici-Olivé and S. Olivé, Trans. Met. Chem., 1 (1976) 109.
5 E.R. Freitas and C.R. Gum, Chem. Engng. Prog., 75 (1979) 73.
6 Y. Chauvin, J.F. Gaillard, D.V. Quang and J.W. Andrews, Chem. Ind. (London), (1974) 375.
7 K.J. Cavell and A.F. Masters, J. Chem. Res., (1983) 72.
8 A.F. Masters and J.K. Cavell, U.S. Pat. 4533651 C.S.I.R.O., 1985.
9 S.J. Brown, L.M. Clutterbuck, A.F. Masters, J.A. Sachinides and P.A. Tregloan, Appl. Catal., in press.
10 S.J. Brown, A.F. Masters and M. Vender, Polyhedron, 7 (1988) 2009.
11 V.W.L. Chin, A.F. Masters, R.J. Tyler and M. Vender, Studies in Surface Science and Catalysis, 36 (1988) 421.
12 B. Bogdanović, B. Spliethoff and G. Wilke, Angew. Chem. Int. Ed. Engl., 19 (1980) 622.
13 K.M. Plowman, Enzyme Kinetics, McGraw-Hill, New York, 1972.
14 R. Chang, Physical Chemistry with Applications to Biological Systems, 2nd edit., Collier MacMillan, New York, 1981.
15 L.M. Clutterbuck, B.Sc.(Hon), Thesis, University of Sydney, 1987.