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Aluminum Halide Effects on Metathesis of 2-Pentene by a Binary Catalyst System of Tungsten Hexachloride and *n*-Butyllithium*

JIN-LIANG WANG, H. R. MENAPACE, AND M. BROWN

Research Division, The Goodyear Tire & Rubber Company, Akron, Ohio 44316

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Metathesis of mixed 2-pentene (46% *trans* and 54% *cis*) by a binary catalyst system of tungsten hexachloride and *n*-butyllithium has been reported to attain the theoretical maximum conversion, 50%, in 4 hr at room temperature. Aluminum halides have exerted substantial effects on this metathesis reaction in the presence of WCl_6 and *n*-BuLi. It has been found that aluminum halide at less than 1 mole/mole of WCl_6 accelerated the formation of 3-hexene and 2-butene in high conversion and selectivity in 15 min reaction time. Beyond this level, conversion was increased at the expense of selectivity.

INTRODUCTION

A homogeneous catalyst system for olefin metathesis has been disclosed by several workers (*1–5*). The preferred catalyst was obtained by the interaction of tungsten hexachloride, ethanol, and ethylaluminum dichloride. Isomerization and oligomerization also occurred when olefins were metathesized over a solid catalyst of molybdenum or tungsten oxides on alumina at temperatures from 90 to 260°C (*6, 7*). At 0°C in chlorobenzene, the catalyst system $Py_2Mo_2\text{–}(NO)_2Cl_2\text{–}EtAlCl_3$ converts 2-pentene into 2-butene and 3-hexene, reaching a maximum conversion of 50% in 10 min (*8*).

In this paper, the effects of aluminum halides on metathesis of 2-pentene by a binary catalyst system of tungsten hexachloride and *n*-butyllithium are described.

EXPERIMENTAL METHODS

Materials and glc Analysis

These were the same as those described in our previous paper (*4*). A mixture of 46% *trans*- and 54% *cis*-2-pentene was used.

Procedure

All the reactions were carried out in 4 oz glass bottles at room temperature. Injections of chemical reagents were done by means of hypodermic syringes. Two orders of injections were used: (1) non-premixing system, that is, WCl_6, mixed 2-pentenes, *n*-BuLi and AlX_3 were added successively; (2) premixing system, that is, WCl_6 and *n*-BuLi were premixed for 10 or 30 min and then 2-pentene and aluminum halide were added successively and reacted for 15 min. In both systems, reaction was terminated with 1 ml of isopropyl alcohol. In all the experiments, ratios of WCl_6/2-pentene/*n*-BuLi were 0.0002/0.01/0.0004. Reaction time began from the time of injection of aluminum halide.

RESULTS

The terms "conversion" and "selectivity" used here have the same meanings as those described in our previous paper (*4*).

1. Non-Premixing System

Without aluminum halide, metathesis of 2-pentenes into 3-hexene and 2-butene by a binary catalyst system of tungsten hexachloride and *n*-butyllithium yielded 10% conversion and 98 mole % total se-

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TABLE 1
EFFECT OF ALUMINUM CHLORIDE

$AlCl_3$, mole	0	.000008	.00004	.00008	.0002	.0003	.0004
Conversion, %	10	18	32	39	61	69	70
Selectivity to 3-hexene, mole %	47	37	35	38	40	31	28
Selectivity to 2-butene, mole %	51	37	37	38	29	19	17
Total selectivity, mole %	98	74	72	76	69	50	45
2-pentene, *trans/cis*	1.2	1.2	1.9	3.2	4.7	5.6	5.2
2-butene, *trans/cis*	0.8	0.9	1.2	1.6	2.5	2.8	2.5

TABLE 2
EFFECT OF ALUMINUM BROMIDE

$AlBr_3$, mole	0	.00005	.0001	.0002	.0003	.0004
Conversion, %	10	12	36	43	64	73
Selectivity to 3-hexene, mole %	47	36	45	39	30	19
Selectivity to 2-butene, mole %	51	38	42	35	23	10
Total selectivity, mole %	98	74	87	74	53	29
2-pentene, *trans/cis*	1.2	1.4	3.0	3.5	6.7	9.0
2-butene, *trans/cis*	0.8	0.8	1.4	1.5	2.5	2.7

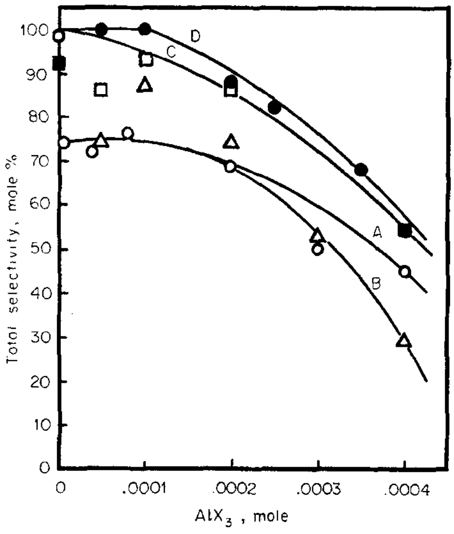


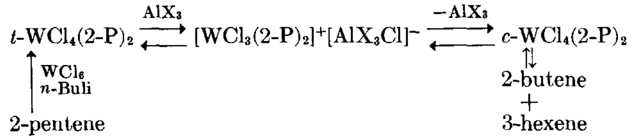
FIG. 1. A plot of total selectivity (mole %) vs AlX_3 (mole): ○, $AlCl_3$ effect on non-premixing system (A); △, $AlBr_3$ effect on non-premixing system (B); □, $AlCl_3$ effect on premixing system (C); ●, $AlBr_3$ effect on premixing system (D).

lectivity in 15 min reaction time. With aluminum halide, conversion was increased at the expense of selectivity. This trend continued with increasing aluminum halide (Tables 1 and 2). The initial rate of reaction appeared to be $AlCl_3 > AlBr_3$. Total selectivities were approximately the same in both $AlCl_3$ and $AlBr_3$ systems. (See Fig. 1, curves A, B.) The high conversions caused by small amount of AlX_3 may be explained by: $WCl_6 + AlX_3 \rightarrow [WCl_5]^+ \cdot [AlX_3Cl]^-$.

2. Premixing System

WCl_6 and *n*-BuLi were premixed for 10 min and then 2-pentenes and AlX_3 were added successively and reacted for 15 min. In both $AlCl_3$ and $AlBr_3$ systems, conversion was increased in a similar way, but total selectivity was much higher than obtained in the non-premixing runs of system (1) (Fig. 1, curves C, D). The initial rate of reaction appeared to be $AlCl_3 >$ $AlBr_3$, but the total selectivity suggested $AlCl_3 \sim AlBr_3$ (Tables 3 and 4).

The prereaction of WCl_6 and *n*-BuLi has allowed the aluminum halides to exert a beneficial influence, possibly by the isomerization of an inactive *trans* tungsten intermediate to a reactive *cis* [see more details in Ref. (*4*)]:



$$\begin{tikzcd} t\text{-}WCl_4(2\text{-}P)_2 \arrow[r, shift left, "AlX_3"] & {[WCl_3(2\text{-}P)_2]^+[AlX_3Cl]^-} \arrow[l, shift left] \arrow[r, shift left, "-AlX_3"] & c\text{-}WCl_4(2\text{-}P)_2 \arrow[l, shift left] \arrow[d, shift left] \\ 2\text{-pentene} \arrow[u, "WCl_6 \ n\text{-}BuLi"'] & & 2\text{-butene} + 3\text{-hexene} \arrow[u, shift left] \end{tikzcd}$$

This benefit is *not* derived from the possible formation of n-BuAlX$_2$ from n-BuLi and AlX$_3$, as shown by the following experiment:

n-BuLi (0.0004 mole) and AlCl$_3$ (0.0001 mole) were premixed for 15 min and then 2-pentenes (0.01 mole) and WCl$_6$ (0.0002 mole) were added successively and reacted for 15 min. This reaction gave 61% conversion and 62 mole % total selectivity, whereas premixing of WCl$_6$ and n-BuLi resulted in 48% conversion but with 93 mole % selectivity (Table 3).

TABLE 3
Effect of Aluminum Chloride

AlCl$_3$, mole	0	.00005	.0001	.0002	.0004
Conversion, %	15	42	48	54	76
Selectivity to 3-hexene, mole %	44	41	50	47	30
Selectivity to 2-butene, mole %	48	45	43	39	24
Total selectivity, mole %	92	86	93	86	54
2-pentene, *trans/cis*	1.2	4.8	5.9	5.2	5.0
2-butene, *trans/cis*	0.8	1.8	2.4	2.6	2.7

TABLE 4
Effect of Aluminum Bromide

AlBr$_3$, mole	0	.00005	.0001	.0002	.00025	.00035	.0004
Conversion, %	15	30	40	51	50	58	58
Selectivity to 3-hexene, mole %	44	49	49	47	41	34	30
Selectivity to 2-butene, mole %	48	51	51	41	41	34	24
Total selectivity, mole %	92	100	100	88	82	68	54
2-pentene, *trans/cis*	1.2	2.6	4.2	4.9	4.6	6.5	5.8
2-butene, *trans/cis*	0.8	1.4	1.8	2.5	2.4	2.3	3.5

The *trans/cis* ratios of residual 2-pentene shown in Tables 1–4 were those found at the end of 15 min reaction time. They increased rapidly with increasing conversion and aluminum halide. Similarly, the *trans/cis* ratios of product 2-butene increased almost linearly with increasing aluminum halide in both non-premixing and premixing systems. While our mechanism described in (*4*) predicts that product olefins should be *cis*, it is actually mostly *trans*. This may be due to more extensive isomerization by cationic aluminum species.

In summary, small amounts of aluminum halides enhance the reactivity of the WCl$_6$-n-BuLi catalyst toward metathesis of 2-pentene, possibly by isomerizing an inactive *trans* intermediate, t-WCl$_4$(2-P)$_2$, to the active *cis* form, c-WCl$_4$(2-P)$_2$. The much higher *trans* isomer than *cis* isomer found in the residual 2-pentene and product 2-butene may well be explained by more extensive isomerization by cationic aluminum species.

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