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Temperature Effects on Metathesis of 2-Pentene by A Binary Catalyst System of Tungsten Hexachloride and *n*-Butyllithium

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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. This reaction, carried out using a steel vessel at 60 to 130°C, reached redistribution equilibrium in several minutes. Except for decreasing selectivity at temperatures above 130°C, the total selectivity to 2-butene and 3-hexene was 100 mole % with ratios of olefin/W = 50, and *n*-BuLi/W = 2.

INTRODUCTION

Studies on temperature effects on metathesis of olefins using molybdenum or tungsten oxides on alumina at 90–260°C and $Py_2Mo_2(NO)_2Cl_2$–$EtAlCl_3$ have been reported by several workers (*1–3*).

Recently, we have described that aluminum halides have exerted substantial effects on metathesis of mixed 2-pentene (46% *trans* and 54% *cis*) by a binary catalyst system of WCl_6–*n*-BuLi at room temperature. At less than 1 mole/mole of WCl_6 it 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 (*4*).

In this paper, the effects of temperature on metathesis of the same system is described.

EXPERIMENTAL METHODS

Materials and Gas–Liquid Chromatography Analysis

These were the same as those described in our previous paper (*5*).

Apparatus and Procedure

All the reactions were carried out in a 30 ml Hoke vessel made of stainless steel, incorporating a heating block surrounding the whole reactor, a thermocouple, and an injection valve for sample injection under nitrogen pressure.

Introduction of reagents into the reactor was done in two steps (see Fig. 1). Using a brass "T" at the top of the addition vessel allowed a slow continuous purge of nitrogen while reagents were syringed into the addition vessel. The T was then capped with a pressure gauge, and the vessel was pressurized with nitrogen. This vessel was then attached to the reactor with suitable Swagelok fittings and valves (flushed carefully with nitrogen through a needle). The reagents were then driven into the reactor by nitrogen pressure. Completion of the addition was indicated by stabilization of the gauge after the drop in nitrogen pressure.

The experimental runs were made by two procedures which gave different results.

Procedure 1. This included four steps: (1) The reactor was heated to a desired temperature; (2) 5 ml of 0.04 *M* WCl_6 (in benzene) and 2.25 ml of 4.5 *M* 2-pen-

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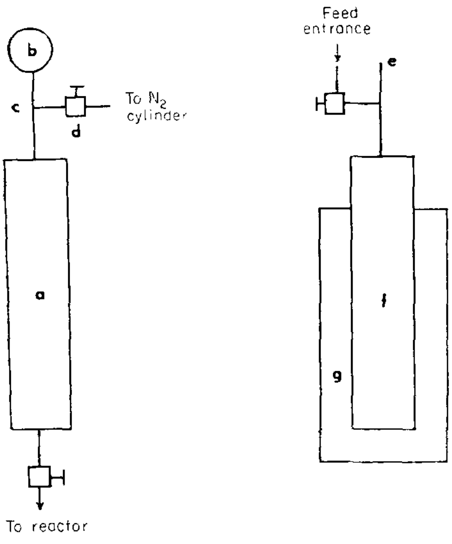

(A) Addition vessel (B) Reactor

FIG. 1. a 30 ml addition vessel; (b) pressure gauge; (c) brass "T"; (d) two-way valve; (e) thermocouple; (f) 30 ml reactor; (g) heating block.

tene (in *n*-pentane) were successively added to the first feed vessel, and 10 ml of 0.04 *M* *n*-BuLi (in benzene) was added to the second one; (3) contents of these two feed vessels were added to the reactor consecutively; and (4) the reaction was terminated by isopropyl alcohol. The average pressure was 400 psig (mostly nitrogen pressure) after the third step. This procedure gave rise to low selectivities in the temperature range 61 to 150°C. Therefore, all the work described in this paper was done by the following procedure.

Procedure 2. In this procedure, WCl_6, 2-pentene, and *n*-BuLi were combined into one feed vessel and then added quickly to the reactor, which was preheated to the chosen temperature. After the reagents were added, the pressure in the reactor was about 210 psig. However, at this point, a valve on the reactor was shut off and the addition vessel and its gauge was removed. Thus, any pressure change in the reactor was not indicated.

Reaction time shown in the tables was counted from the time of introduction of the combined WCl_6, 2-pentene, and *n*-BuLi into the reactor, whereupon the reaction mixture was agitated on a Burrell shaker. After a chosen reaction time was reached, reaction was stopped by injecting 1 ml of isopropyl alcohol into the reactor. Then the heating block was removed and the reactor cooled in dry ice for 1 hr before analysis by gas–liquid chromatography (GLC).

RESULTS

The terms "conversion" and "selectivity" used here have the same meanings as those described in our previous paper (*5*).

Increasing temperature markedly increased the rate of metathesis as shown in Table 1. The reaction rate at 61, 94 and 130°C appeared to be much greater than that at 25°C (*5*). Reaction at 60°C leveled off after 43% conversion in 1 min, at 94°C after 47% conversion in 2 min, and at 130°C after 49% conversion in 10 min. These results may be explained in terms of deactivation of the catalyst with increasing temperature and reaction time.

It was surprising to find that ratios of *trans/cis* in product 2-butene were nearly independent of temperature in the range 61, 94, and 130°C. These data are illustrated in Fig. 2. At 50% conversion (i.e., the point of equilibrium for the redistribution of alkylidene groups), the *trans/cis* ratio for product 2-butene at 25°C is 2.5; at 61, 94, and 130°C, the ratio is 1.6. One would expect each curve to reach its own thermodynamic *trans/cis* equilibrium at its respective temperature. The fact that the reactions at 61 to 130°C converge at *trans/cis* of 1.6 indicates substantial kinetic control at these temperatures, i.e., the rate of reaction is so fast that a higher proportion of the *cis*-2-butene is retained in the product, as might be expected from the $W^{IV}Cl_4 \cdot 2$ olefin intermediate postulated earlier (*5*).

Similar reasoning may also be applied to the case of residual pentenes. The *trans/cis* ratios increased with conversion (Fig. 3). The equilibrium *trans/cis* ratio decreased from 4.2 at 25°C to an average value of 2.5 at 61–130°C.

Total selectivities of nearly 100 mole % were obtained at temperatures up to 130°C, beyond which total selectivity decreased

TABLE 1
EFFECT OF TEMPERATURE

Temp (°C):	25					61				94				130				
Reaction time (sec)	900	1800	3600	7200	14,400	30	60	120	240	30	60	120	240	30	60	120	240	600
Conversion (%)	15	23	40	43	51	34	40	43	43	24	28	47	48	14	20	23	37	49
Selectivity to 3-hexene (mole %)	47	48	49	48	48	48	48	48	42	48	44	48	48	48	48	46	47	45
Selectivity to 2-butene (mole %)	51	52	51	50	51	52	52	52	46	52	56	52	52	52	52	51	51	49
Total selectivity (mole %)	98	100	100	98	99	100	100	100	88	100	100	100	100	100	100	97	98	94
2-Pentene, *trans/cis*	1.2	1.5	2.6	3.0	4.2	1.9	2.4	2.1	1.8	1.3	1.4	2.2	2.2	1.1	1.1	1.2	1.5	2.3
2-Butene, *trans/cis*	0.8	0.9	1.4	1.6	2.5	1.1	1.2	1.4	1.2	1.0	1.0	1.4	1.5	0.9	1.0	1.0	1.2	1.6

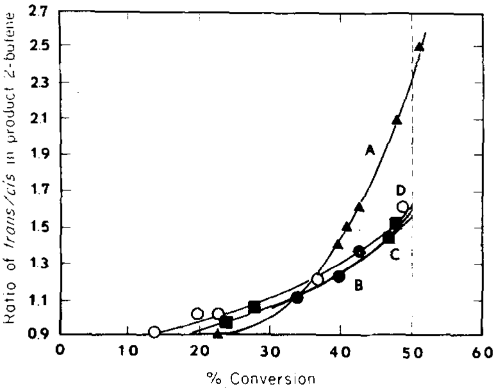

FIG. 2. A plot of isomerization in product 2-butene vs percentage conversion: (▲) 25°C [data from Ref. (5)]; (●) 61°C; (■) 94°C; (○) 130°C.

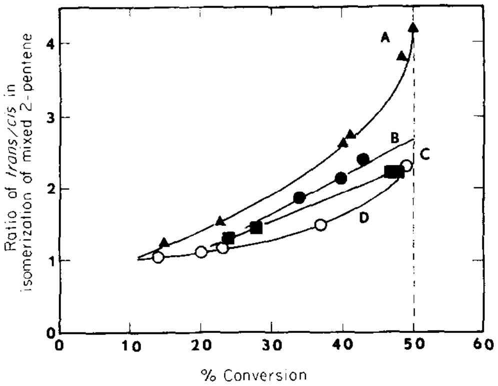

FIG. 3. A plot of isomerization of mixed 2-pentenes vs percentage conversion: (▲) 25°C [data from Ref. (5)]; (●) 61°C; (■), 94°C; (○), 130°C.

sharply (Table 2). Premixing WCl_6, 2-pentene, and n-BuLi before injecting into the reactor may lead to incipient formation of an intermediate species, $W^{IV}Cl_4 \cdot 2$ olefin (5, 6), which may be responsible for the metathesis reaction, giving rise to the results above. Above 130°C, total selectivity decreased to 40 mole %. This is probably due to thermal destruction of the specific intermediate just mentioned.

At about 30-sec reaction time, the rate of reaction apparently decreased with increasing temperature to a minimum value, 14% (Table 2). This could be due to deactivation of the metathesizing catalytic intermediate with increasing temperature. However, above 130°C, oligomerization or polymerization predominates.

It is our conclusion that the rate of metathesis reaction can be greatly accelerated by increasing temperature up to 130°C. Beyond this temperature, the WCl_6 or $W^{IV}Cl_4 \cdot 2$ olefin intermediate possibly responsible for metathesis may be destroyed partially or completely, leading to lower selectivity for the desired products.

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TABLE 2
EFFECT OF TEMPERATURE ON CONVERSION AND SELECTIVITY

Temp (°C):	61	94	113	130	150	170
Conversion[a] (%)	34	24	15	14	15	24
Selectivity to 3-hexene (mole %)	46	48	48	48	20	20
Selectivity to 2-butene (mole %)	50	52	50	52	22	20
Total selectivity, mole %	96	100	98	100	42	40
2-Penetene, trans/cis	1.6	1.1	1.1	1.0	1.0	1.0
2-Butene, trans/cis	1.0	0.9	0.8	0.7	0.7	0.8

[a] At about 30-sec reaction time.