

## Solvent Effects on the Isomerization of 1-Pentene Catalyzed by Cationic Platinum Complexes

Hiroyoshi KANAI\* and Osamu HIRAKO†

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606

(Received September 7, 1981)

**Synopsis.** The isomerization of 1-pentene with  $[\text{PtH}(\text{PPh}_3)_3]\text{X}$  ( $\text{X}=\text{SO}_4\text{H}$ ,  $\text{ClO}_4$ ) occurred only in ethers. The decrease in the concentrations of 1-pentene and the platinum complexes leads to high *cis*-selectivity.

Wells *et al.* deduced that stereoselectivity in the isomerization of 1-alkenes was determined by the degree of molecular congestion at a catalyst site:<sup>1,2)</sup> the preferential *cis*-alkene formation occurred when the site of catalytic activity was highly congested.<sup>1–3)</sup> A wide range of metal-phosphine complexes catalyze 1-pentene isomerization to 2-pentenes *via* the formation of secondary pentyl intermediates with preferential formation of *cis*-2-pentene.<sup>2–5)</sup> The selectivity was explained in terms of the restriction of the normal rotations in the secondary pentyl intermediate by phosphine ligands as low the conformation of molecular volume predominates as possible.<sup>1,2)</sup> We observed selective *cis*-isomerization of 1-pentene catalyzed by  $\text{NiX}(\text{PPh}_3)_3\text{--SnCl}_2$  ( $\text{X}=\text{halogen}$ ) systems which was attributed to the bulkiness and *trans*-effect of  $\text{SnCl}_2\text{X}^-$  ligands.<sup>4)</sup>

$[\text{PtH}(\text{PPh}_3)_3]\text{X}$  ( $\text{X}=\text{SO}_4\text{H}$ ,  $\text{ClO}_4$ ) isomerized 1-pentene slowly at 50 °C to give 2-pentene having an initial *cis/trans* ratio of more than 3 only in ethers (Table 1). No isomerization occurred with  $[\text{PtH}(\text{PPh}_3)_3]\text{SO}_4\text{H}$  in homogeneous solutions of ethyl methyl ketone, methanol, *N,N*-dimethylformamide, acetonitrile, and nitromethane, or in a heterogeneous solution of benzene. However, in homogeneous solutions of benzene and dichloromethane, or in heterogeneous

solutions of dioxane, THF, and 1,2-dimethoxyethane (glyme) the isomerization of 1-butene<sup>6)</sup> or 1-pentene<sup>7)</sup> with  $\text{PtH}(\text{PPh}_3)_2\text{ClO}_4$  proceeded readily in preferential formation of the *trans*-isomers. The initial *trans/cis* ratio in glyme (Table 1) is in excess of the equilibrium value as is only known in cases of the isomerization of 1-pentene catalyzed by  $\text{Pt(II)–SnCl}_2$  complex,<sup>8)</sup>  $\text{RuH}_4(\text{PPh}_3)_3$ , and  $\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3$ .<sup>9)</sup>  $[\text{PtH}(\text{PPh}_3)_3]\text{ClO}_4$  (tris-complex) is lower in reactivity and higher in *cis*-selectivity than  $\text{PtH}(\text{PPh}_3)_2\text{ClO}_4$  (bis-complex). Although relative rates are not determined exactly owing to the heterogeneity, isomerization proceeds favorably in glyme among ethers investigated. First-order dependency and constant *cis/trans* ratios were observed in ethers listed in Table 1. When excess of  $\text{PPh}_3$  was added to the bis-complex, there appeared reaction features characteristic of the tris-complex: the *cis/trans* ratios increased gradually from 0.55 to 0.99, 2.00 and 2.70 in accordance with excess  $\text{PPh}_3/\text{bis-complex}=0.85, 0.90, 0.95$ , and  $0.97$ , respectively.

The isomerization catalyzed by the tris-complex occurs *via* a metal-hydride addition-elimination mechanism: (1)  $\text{Pt–H}$  bond was detected in the IR spectrum after isolation of the catalyst from the reaction mixture of  $[\text{PtD}(\text{PPh}_3)_3]\text{ClO}_4$  and 1-pentene in glyme; (2) intermolecular hydrogen transfer between  $\text{C}_2\text{D}_4$  and  $\text{C}_2\text{H}_4$  occurred.

The lower the concentrations of 1-pentene and of the platinum complex become, the higher *cis*-selectivity rises (Fig. 1). The increase of 1-pentene results in the dissociation of the tris-complex to give

TABLE 1. ISOMERIZATION OF 1-PENTENE CATALYZED BY PLATINUM COMPLEXES IN ETHERS

Catalyst	Solvent	Temp °C	Time min	Conversion %	<i>cis/trans</i>	
$[\text{PtH}(\text{PPh}_3)_3]\text{SO}_4\text{H}^{\text{a)}$	Dioxane	50	240	3.5	4.12	Heterogeneous
	THF	50	240	8.3	3.49	Heterogeneous
	Anisole	50	240	0.8	5.84	Heterogeneous
	Glyme	50	240	15.1	4.25	Heterogeneous
$[\text{PtH}(\text{PPh}_3)_3]\text{ClO}_4^{\text{b)}$	Dioxane	50	240	0.5	4.97	Heterogeneous
	THF	50	240	2.5	6.72	Heterogeneous
	Anisole	50	240	1.4	4.83	Homogeneous
	Glyme <sup>c)</sup>	50	240	8.3	4.24	Heterogeneous
$[\text{PtH}(\text{PPh}_3)_2\text{ClO}_4^{\text{d)}$	Dioxane	r. t.	10	29.5	0.23	Heterogeneous
	THF	r. t.	30	6.0	0.32	Heterogeneous
	Glyme	r. t.	5	4.7	0.13	Heterogeneous
	Glyme <sup>e)</sup>	50	240	90.0	0.55	Heterogeneous
	Glyme <sup>f)</sup>	50	240	2.4	2.70	Heterogeneous

a)  $[\text{Pt}]$  0.1 mmol, [1-pentene] 10 mmol, solvent 20 ml. b)  $[\text{Pt}]$  0.05 mmol, [1-pentene] 5 mmol, solvent 10 ml.

c)  $[\text{Pt}]$  0.025 mmol, [1-pentene] 5 mmol, glyme 10 ml. d)  $[\text{Pt}]$  0.05 mmol, [1-pentene] 5 mmol, solvent 10 ml.

e) Addition of excess  $\text{PPh}_3/\text{Pt}=0.85$ . f) Addition of excess  $\text{PPh}_3/\text{Pt}=0.97$ .

† Present address: Mitsubishi Motors Corporation, Kyoto Works, Ukyo-ku, Kyoto 615.

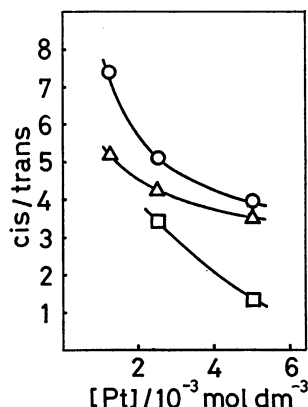


Fig. 1. Plots of *cis*-selectivity vs. the concentration of  $[\text{PtH}(\text{PPh}_3)_3]\text{ClO}_4$ . The ratios of 1-pentene to the Pt complex: 10 (○); 20 (△); 100 (□).

the bis-complex which is high in catalytic activity and low in *cis*-selectivity. Conversions of 1-pentene after 4 h at 10, 20, and 100 of 1-pentene/Pt ratios were 8.6, 10.0, and 11.9%, respectively in  $5 \times 10^{-3}$  mol dm<sup>-3</sup> of  $[\text{PtH}(\text{PPh}_3)_3]\text{ClO}_4$ . The opposite tendency in regard to the effect of the concentration of catalysts would be attributed to a gradual increase in the degree of dissociation of the catalyst by losing  $\text{PPh}_3$  ligands.<sup>3)</sup> The rise in the *cis/trans* ratio with decreasing catalyst concentration in Fig. 1 would be due to the lack of dissociation of the tris-complex in ethers.

The presence of compounds having an ether linkage is essential for catalytic activity of the tris-complex. Diallyl ether and allyl phenyl ether were isomerized by the tris-complex in neat liquid or a non-ether solvent such as ethyl methyl ketone. No isomerization of allylbenzene occurred in neat liquid but it was isomerized to propenylbenzene in glyme.

### Experimental

1-Pentene was obtained from Tokyo Kasei Kogyo Co.

and distilled prior to use. Tetrahydrofuran, dioxane, and glyme were refluxed over sodium, distilled and stored in a nitrogen atmosphere. Other chemicals were commercial materials and used without further purification.

$[\text{PtH}(\text{PPh}_3)_3]\text{X}$  ( $\text{X}=\text{SO}_4\text{H}$ ,  $\text{ClO}_4$ )<sup>10)</sup> and  $\text{PtH}(\text{PPh}_3)_2\text{ClO}_4$ <sup>11)</sup> were prepared according to the methods given in the literature.

**Procedure.** A two-necked 100 ml flask was charged in a nitrogen atmosphere with  $(2.5\text{--}10) \times 10^{-4}$  mol of a platinum complex, (10–20) ml of dry, degassed solvent, and a micro stirring bar. The flask was cooled in liquid nitrogen and evacuated, and  $(5\text{--}10) \times 10^{-3}$  mol of 1-pentene was added. The flask was immersed in a bath maintained at 50 °C or r.t. Samples of the solution, ca. 0.1 ml, were withdrawn through the side arm at intervals with a syringe and the distillates obtained from thaw-to-thaw distillation were analyzed by a Shimadzu GC gas chromatograph on the 2,4-dimethylsulfolane (30%)/C-22 column operated at ambient temperature.

### References

- 1) D. McMunn, R. B. Moyes, and P. B. Wells, *J. Catal.*, **52**, 472 (1978).
- 2) D. Bingham, D. E. Webster, and P. B. Wells, *J. Chem. Soc., Dalton Trans.*, **1974**, 1514.
- 3) D. Bingham, D. E. Webster, and P. B. Wells, *J. Chem. Soc., Dalton Trans.*, **1974**, 1519.
- 4) H. Kanai, K. Kushi, K. Sakanoue, and N. Kishimoto, *Bull. Chem. Soc. Jpn.*, **53**, 2711 (1980).
- 5) F. Pennella, *J. Organomet. Chem.*, **78**, C10 (1974).
- 6) H. C. Clark and H. Kurosawa, *Inorg. Chem.*, **12**, 1566 (1973).
- 7) O. Hirako, MA Dissertation, Kyoto University 1975.
- 8) G. C. Bond and M. Hellier, *Chem. Ind. (London)*, **1965**, 35; *J. Catal.*, **7**, 217 (1967).
- 9) F. Pennella and R. L. Banks, *J. Catal.*, **35**, 73 (1974).
- 10) F. Cariati, R. Ugo, and F. Bonati, *Inorg. Chem.*, **5**, 1128 (1966).
- 11) I. V. Gavrilova, M. I. Gel'fman, N. V. Ivannikova, and V. V. Razumovskii, *Zh. Neorg. Khim.*, **16**, 1124 (1971).