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HOMOGENEOUS ISOMERIZATION AND HYDROGENATION OF 1-PENTENE CATALYZED BY PLATINUM COMPLEXES

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Isomerization and hydrogenation reactions of 1-pentene were catalyzed by zerovalent Pt complex, $Pt(Pph_3)_3$, in the presence of $SnCl_2$, oxygen, aldehyde, and $[PtH(Pph_3)_3]X$ ($X=HSO_4$, NO_3, ClO_4) under mild conditions.

It is known that unsaturated compounds are hydrogenated and isomerized by platinum complexes of H_2PtCl_2 and $PtX_2(Pph_3)_2$ in the presence of $SnCl_2$ and H_2,1),2) and that zerovalent platinum complex, $Pt(Pph_3)_3$, hydrogenates olefins at 175°C and 100 atm pressure in benzene.3) We have been researching those reactions in other catalytic systems and have found some new results. Thus, $Pt(Pph_3)_3$ in the presence of $SnCl_2$, O_2, or n-butyraldehyde were effective for catalytic isomerization and hydrogenation of 1-pentene under mild conditions. Furthermore, cationic complexes, $[PtH(Pph_3)_3]X$ ($X=HSO_4$, NO_3, ClO_4), obtained from $Pt(Pph_3)_3$ and HX,4) exhibited slight catalytic activity for those reactions.

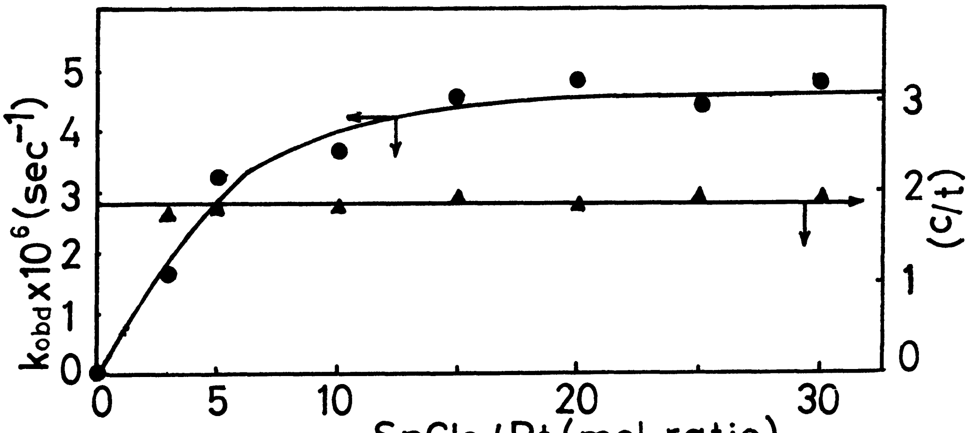

Fig. 1. Effect of $SnCl_2$ on isomerization of 1-pentene with $Pt(Pph_3)_3$ in H_2 atmosphere.

The ratio of cis-2-pentene to trans-2-pentene was always constant at any ratio of $SnCl_2/Pt$. The high cis-selectivity was characteristic in comparison with that of isomerization by $PtCl_2(Pph_3)_2$-$SnCl_2$,$^{1)}$ H_2PtCl_6-$SnCl_2$,$^{2)}$ which gave nearly equilibrium ratio. $Pt(Pph_3)_4$ was less active than $Pt(Pph_3)_3$ as shown in Table I. This fact suggests that active species is Pt complex in which Pph_3 was dissociated from $Pt(Pph_3)_4$.

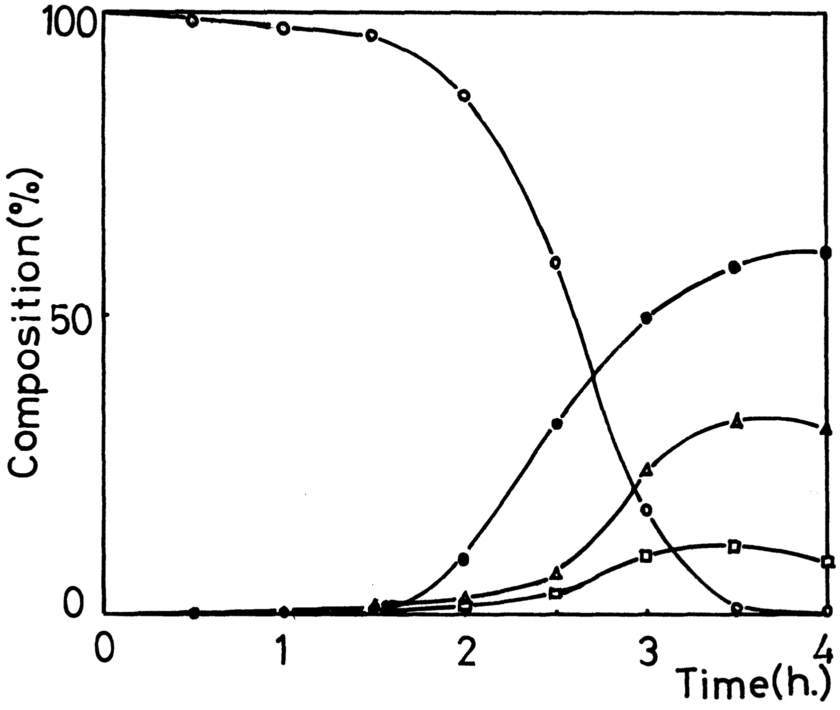

Fig. 2. Hydrogenation and isomerization of 1-pentene using $Pt(Pph_3)_3$ in H_2 containing a small amount of O_2.
Solvent THF 20 ml, 1-pentene 10 mmole, $Pt(Pph_3)_3$ 0.10 mmole, at 50°C. ●: pentane; o: 1-pentene; Δ: trans-2-pentene; ◘ : cis-2-pentene.

The active species of Pt^0 complex-$SnCl_2$ is different from that of Pt^{II} complex-$SnCl_2$, because of the dissimilality of cis-selectivity. The $Pt(Pph_3)_3$-$SnCl_2$ system catalyzed isomerization in preference to hydrogenation in an atmosphere of hydrogen, but when the used hydrogen contained a small amount of oxygen, 1-pentene was remarkably hydrogenated by $Pt(Pph_3)_3$ even in the absence of $SnCl_2$, as shown in Table I and Fig. 2. Isomerization and hydrogenation were accelerated after two hours, and at the same time the color of the reaction mixture changed from light yellow to dark brown. The induction period and the rate of hydrogenation were dependent on the amount of oxygen. Hydrogenation occurred preferentially in contrast with the result by $Pt(Pph_3)_3$-$SnCl_2$.

When small amounts of n-butyraldehyde were added in a solution of $Pt(Pph_3)_3$, 1-pentene was also hydrogenated a little, and a trace of isomerized olefins were formed.

$Pt(Pph_3)_3$ itself had no catalytic activity for hydrogenation and isomerization of 1-pentene at 50° under ambient pressure in THF. However, those reactions of 1-pentene were found to occur when $SnCl_2$ was added to $Pt(Pph_3)_3$. Isomerization did not necessarily require the presence of hydrogen, though it was found that hydrogen accelerated the reaction. The observed 1st order rate constants of isomerization increased with the amount of $SnCl_2$, and reached a constant in the range of $SnCl_2/Pt \geqq 10$, as shown in Fig. 1.

Table I. Hydrogenation and Isomerization of 1-pentene using platinum complexes.[a]

Catalysts	Additives	Products' composition(%)[b]				cis/trans	Atmosphere
		pentane	1-pentene	trans-2-pentene	cis-2-pentene		
$Pt(Pph_3)_3$	$SnCl_2$ 1.0 mmole	—	89.0	3.80	7.27	1.91	N_2
		0.84	85.7	4.71	8.77	1.86	H_2
$Pt(Pph_3)_3$	Small amount of O_2	60.6	0.67	30.1	8.60	0.26	H_2
$Pt(Pph_3)_3$	n-Butyraldehyde	2.81	97.0	0.08	0.05	0.58	H_2
$[PtH(Pph_3)_3]\cdot HSO_4$		0.03	87.3	2.61	10.0	3.87	N_2
		0.62	95.1	1.09	3.16	2.90	H_2
$[PtH(Pph_3)_3]\cdot NO_3$		—	99.8	0.11	0.11	0.95	N_2
		0.30	99.4	0.12	0.17	1.36	H_2
$[PtH(Pph_3)_3]\cdot ClO_4$		—	86.9	2.05	5.55	2.71	N_2
		0.88	98.7	0.10	0.31	3.22	H_2
$Pt(Pph_3)_4$	$SnCl_2$ 1.0 mmole	—	93.0	2.45	4.55	1.87	N_2
		0.19	90.4	3.31	6.13	1.85	H_2
$PtCl_2(Pph_3)_2$	$SnCl_2$ 1.0 mmole	—	99.4	0.56			N_2
		6.47	6.34	65.4	21.7	0.33	H_2

(a) Conditions: 1-pentene 10 mmole, platinum complexes 0.10 mmole [olefin/catalyst (mole ratio=100)], solvent THF 20 ml, at 50°C.

(b) Composition of products after 4 hours.

$[PtH(Pph_3)_3]X$ ($X=HSO_4$, NO_3, ClO_4) catalyzed isomerization of 1-pentene, in which catalytic activity and cis-selectivity were affected by anions. Hydrogenation took place scarcely in an atmosphere of hydrogen, which inhibited isomerization.

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