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Homogeneous Catalysis by Noble Metal Salts

II. Isomerization of 1-Pentene by a Platinum(II)–Tin(II) Complex

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In the presence of hydrogen and a Pt^{II}-Sn^{II} complex, 1-pentene isomerizes at room temperature to a mixture of 2-pentenes in which the *trans* isomer predominates (~85%); the yield of this isomer increases with decreasing temperature. The rate of hydrogenation, which is slow, is proportional to the instantaneous concentration of 1-pentene, and virtually no hydrogenation occurs with *cis*-2-pentene. Styrene is hydrogenated slowly. The rates of both isomerization and hydrogenation are maximum at a Sn/Pt ratio of about 12.

The reaction is thought to proceed by addition of 1-pentene to a hydride formed from *trans*-$[Pt(SnCl_3)_2Cl_2]$ and hydrogen. The high *trans/cis* ratio in the 2-pentene formed is interpreted semiquantitatively by a conformational analysis of the resulting 2-pentyl radical. Pentane is formed by hydrogenolysis of the 1-pentyl–Pt bond.

INTRODUCTION

Of the several noble metal salts and complexes known to catalyze the homogeneous hydrogenation of olefins, the complex formed from hexachloroplatinate(IV) ion and tin(II) chloride in methanol is one of the most active (*1*). Although the nature of the catalytically active species has not yet been firmly established, a number of salts containing platinum and tin in the anion have been described in solution (*2*) and have been isolated as salts with bulky cations (NR_4^+, PR_4^+; R = alkyl or aryl) (*1*, *2*, *3*). Complexes of other Group VIII metals with tin(II) chloride have been described (*2*, *4*) but have not been found to have catalytic activity.

NMR examination of the interaction of ethylene with the platinum-tin complex suggested (*1*) an extremely rapid exchange between free and coordinated ethylene, and hence it was reasonable to expect to observe the process of double-bond migration in higher olefins. This expectation was fulfilled and we now report our study of the hydrogenation and isomerization of 1-pentene catalyzed by this complex; a preliminary note has already appeared (*5*).

EXPERIMENTAL

Catalyst solutions were prepared, without exclusion of air unless the contrary is noted, by dissolving $SnCl_2{\cdot}2H_2O$ in methanol and adding the required volume of aqueous chloroplatinic acid solution. A typical solution contained 10 mmoles $SnCl_2{\cdot}2H_2O$ in 20 ml of methanol and 2 mmoles of H_2PtCl_6 in 2 ml of aqueous solution. Solutions were deep red in color and darkened on standing; they were normally used about 30 min after preparation (see below).

Reactions were performed in a 20 ml round-bottomed flask fitted with a sidearm sealed by a serum cap through which samples could be withdrawn for analysis. The flask, immersed in a thermostatically controlled water bath, was connected to a gas-burette system and after it had been thoroughly purged with hydrogen the liquids were injected into the flask in the sequence: solvent (methanol), 1-pentene, catalyst solution. The total volume of liquid was 5 ml.

The flask was then vigorously agitated (usually 1250 min^{-1}) and stopped only when samples were being extracted. GLC analysis employed a 4-m column of 20% $AgNO_3$ in benzyl cyanide on 44–60 mesh Silocel at room temperature.

RESULTS

Preliminary experiments showed that no reaction occurred in the absence of hydrogen or of tin(II) chloride. In the presence of hydrogen the main reaction was isomerization and [as expected (*1*)] very little hydrogenation took place, the concentration of *n*-pentane never exceeding 5% of the total hydrocarbon. Rate constants quoted below are derived from generally satisfactory first order plots of 1-pentene removal, and are uncorrected for this small amount of hydrogenation.

Much trouble was experienced in obtaining reproducible rates, despite the many precautions taken. In a small number of experiments, abnormally fast rates were observed; these were possibly caused by the formation of very finely divided platinum, although there were no visible signs of this and the product distribution was the same as in experiments giving the more usual slower rates. Preparation of the catalyst solution in the reaction vessel under hydrogen did not change the rate from its normal value. For the present purposes, the experiments giving the fast rates have been ignored.

The activity of catalyst solutions prepared in air varied with the time which elapsed before use, as follows (T = 25°C; 1-pentene, 2.28 M; Pt, 3.26×10^{-3} M; Sn, 38.4×10^{3} M):

Time after mixing (hr)	0	0.5	4.5	27
$10^3 k$ (min^{-1})	19.6	46.1	41.5	34.6

Solutions were therefore used about 30 min after preparation. The composition of the products (see below) was however approximately constant. Experiments performed using an agitation frequency of 1075 min^{-1} instead of the usual 1250 min^{-1}, other conditions being as above, gave rate constants ($\times 10^3$) of 41.5 and 43.8 min^{-1}; reactions at the higher agitation frequency are therefore free from diffusion limitation.

In an attempt to define the stoichiometry of the catalytically active species, experiments were performed using a fixed Sn concentration (5.75×10^{-2} M) and Pt concentrations between 2.44×10^{-3} and 9.76×10^{-3} M (T = 25°C; 1-pentene, 2.28 M). The results are shown in Fig. 1; maximum rates resulted with a Sn/Pt ratio of 11.8. Rates of hydrogenation (as measured by the *n*-pentane concentration) after 30 min paralleled the isomerization rates (see Fig. 2).

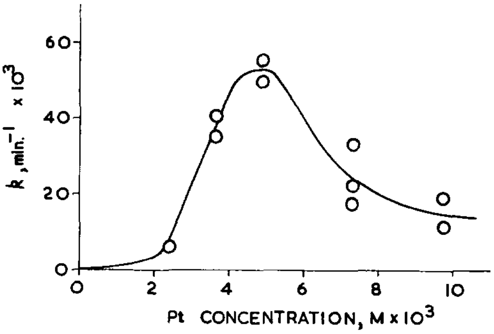

FIG. 1. Dependence of rate constant for isomerization on Pt concentration at constant Sn concentration (5.75×10^{-2} M).

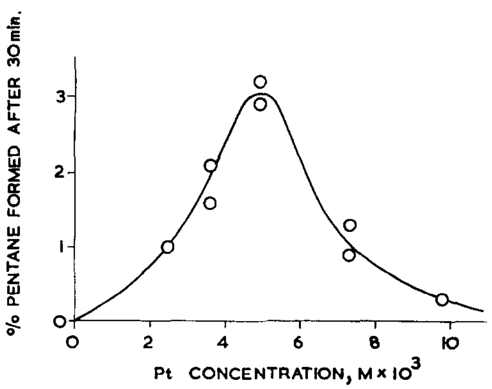

FIG. 2. Dependence of rate of hydrogenation (as measured by *n*-pentane yield after 30 min) on Pt concentration at constant Sn concentration.

PRODUCT COMPOSITION

The chief product of the isomerization is *trans*-2-pentene (see Fig. 3). The "*trans* isomer yield" is defined as 100 × *trans*-2-pentene/total 2-pentene; its value when the two 2-pentene isomers are in equilibrium is

82.2%, but the observed value was almost always greater. Several methods of determining this quantity were tried, including (i) averaging all values through the course of the experiment, (ii) drawing initial tangents to composition–time plots, and (iii) measuring slopes of semilogarithmic plots of product concentrations versus time; all gave the same values within experimental error (e.g., 87.5%, 87.2%, 85.8%). In three experiments carried out at 18.5°C with a Pt concentration either 7.32×10^{-3} or 9.76×10^{-3} *M* (other conditions being as in the last paragraph), the averages of the *trans*-isomer yields obtained by the three methods were 86.7%, 87.4%, and 85.7%. There was no significant variation of the *trans*-isomer yield with variation of Pt concentration.

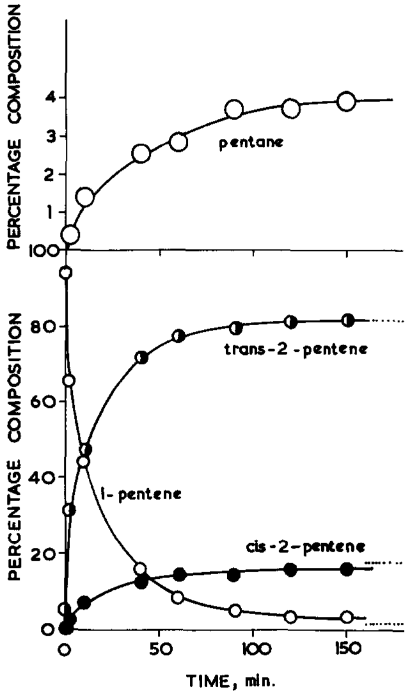

FIG. 3. Dependence of product composition on time (1-pentene = 2.28 *M*; Pt = 4.9×10^{-3} *M*; Sn = 5.75×10^{-2} *M*; 25°C).

The rate of formation of *n*-pentane was always observed to decrease through the course of an experiment (see Fig. 3) and by using the method of tangents the rate was established to be proportional to the instantaneous 1-pentene concentration. It therefore appears that 1-pentene is much more easily hydrogenated than the 2-pentene isomers. This was confirmed by taking 2-pentene (93% *cis*, 7% *trans*) and observing that although the rate constant for isomerization was 28.7×10^{-3} min^{-1}, only 0.2% *n*-pentane was formed after 30 min.

To confirm that only molecules having double bonds in terminal positions are susceptible to hydrogenation by this catalyst, we briefly examined the behavior of styrene, where the double bond is incapable of movement. At 18°C with a styrene concentration of 2.18 *M*, an Sn concentration of 5.75×10^{-2} *M* and a Pt concentration of 4.88×10^{-3} *M*, rates of hydrogen uptake of about 0.25 ml min^{-1} were recorded. GLC analysis confirmed that hydrogenation to ethylbenzene was indeed occurring. Slower rates were observed when either higher or lower Pt concentrations were employed; in this respect the behavior of styrene is similar to that of 1-pentene.

In addition to the results obtained in the region of room temperature, experiments were also performed under standard conditions (Pt = 4.88×10^{-3} *M*, Sn = 5.75×10^{-2} *M*) at −7°, 0.5°, and 40°C. Rates were not sufficiently reliable to yield an accurate activation energy, but there was a consistent trend in the *trans*-isomer yield, as follows:

Temp. (°C)	−7°	0.5°	18.5°	40°
Trans-isomer yield (%)	89.9	88.2	86.5	85.1

From these results we deduce that the activation energy for forming the *trans* isomer is 1.4 ± 0.2 kcal mole^{-1} less than for forming the *cis* isomer. At temperatures above about 80–90°C we would expect the two isomers to be formed in their thermodynamic equilibrium proportions. The activation energy for hydrogenation appeared to be similar to that for isomerization.

DISCUSSION

In confirmation of previous work (*1*), we have observed that the hydrogenation of 1-pentene catalyzed by the platinum(II)–tin(II) complex is very slow, although under our conditions quite rapid isomerization to a mixture of 2-pentene isomers occurs.

An understanding of the mechanism of the hydrogenation and isomerization of 1-pentene catalyzed by the platinum(II)–tin(II) complex requires a knowledge of the one or more species in solution having catalytic properties. We consider first those salts which have been isolated, including those of other Group VIII metals besides platinum. The dimeric rhodium(I) salt, $(NR_4^+)_4[RhSn_2Cl_7]_2^{4-}$, has been assigned a symmetrical chloride-bridged structure *(2)*, as has the analogous arsonium salt of Pd(II) *(4)*. Monomeric complex ions formulated as $[Ru^{II}(SnCl_3)_2Cl_2]^{2-}$, $[Ir^{III}(SnCl_3)_2Cl_3]_2^{4-}$, and $[Pt^{II}(SnCl_3)_2Cl_2]^{2-}$ have also been isolated as their alkylammonium salts *(2)*. Cramer *et al.* have also isolated the latter ion as its phosphonium salt *(1)*, and additionally have made a salt of the ion $[Pt(SnCl_3)_5]^{3-}$ and have determined its structure to be trigonal bipyramidal *(3)*. By treating this with hydrogen at 500 atm, they have formed the ion $[HPt(SnCl_3)_4]^{3-}$ and have followed its formation under milder conditions.

The ion $[Pt(SnCl_3)_2Cl_2]^{2-}$ exists as *cis* and *trans* isomers *(2)*. A yellow salt $(NR_4^+)_2[Pt(SnCl_3)_2Cl_2]^{2-}$, precipitated from sodium chloroplatinate and tin(II) chloride (Pt/Sn, 1:2) in ethanol by NR_4Cl, is believed to be the *cis* isomer; under other conditions a red salt, believed to be the *trans* isomer, is obtained. This latter form predominates in fresh solutions at room temperature and also in aged solutions when the Sn/Pt ratio exceeds 2; when the ratio exceeds 8 it is the only detectable form. The *cis* isomer is the more thermodynamically stable although the formation of the *trans* isomer is kinetically favored, due to the *trans* effect of the $SnCl_3^-$ being greater than for Cl^- after one substitution *(6)*. The stability of the *trans* isomer in solutions containing excess tin(II) chloride is due to the suppression of the dissociation necessary for isomerization.

There is some confusion concerning the nature of salts precipitated at high Sn/Pt ratios. Doubt has been expressed *(2)* as to whether the ion $[Pt(SnCl_3)_5]^{3-}$ exists in solution, and our further discussion will proceed on the assumption that *trans*-$[Pt(SnCl_3)_2Cl_2]^{2-}$ is the principal active species. It is possible that the low activity of solutions in which Sn/Pt is less than about 8 is due to the occurrence in them of the *cis* isomer which could be less reactive because of its greater stability. Similarly the decrease in activity at high Sn/Pt ratios could be due to the existence of the $[Pt(SnCl_3)_5]^{3-}$ ion, although Cramer *et al.* have hinted *(7)* that the derived hydride (see above) is the active species.

The *trans*-isomer yield is independent of the Sn/Pt ratio and of the age of the catalytic solution, suggesting that there is only one active species present. The scheme originally proposed *(5)* can now therefore be specified as follows:

$$[Pt(SnCl_3)_2Cl_2]^{2-} + H_2 \rightarrow [HPt(SnCl_3)Cl_2]^{2-} + H^+ + SnCl_3^- \quad (1)$$

$$[HPt(SnCl_3)Cl_2]^{2-} + C_5H_{10} \rightleftarrows [C_5H_{11}Pt(SnCl_3)Cl_2]^{2-} \quad (2, 2')$$

$$[C_5H_{11}Pt(SnCl_3)Cl_2]^{2-} + H_2 \rightarrow [HPt(SnCl_3)Cl_2]^{2-} + C_5H_{12} \quad (3)$$

All the anions are supposed to have a *trans* configuration. Evidence for step (1) comes from the recent work of Cramer *et al.* *(3)*, although they used a different anion. The olefin insertion reactions analogous to step (2) have been proposed to interpret the hydrogenation of butadiene and other conjugated dienes catalysed by the pentacyanocobaltate ion $[Co(CN)_5]^{3-}$ and have been confirmed by observing *(7)* the insertion of C_2F_4:

$$[HCo(CN)_5]^{3-} + C_2F_4 \rightarrow [HCF_2CF_2Co(CN)_5]^{3-}$$

Isomerization occurs by step (2) as discussed below and hydrogenation by step (3), with the regeneration of the original hydride.

The hydrogenation rate varied with the Sn/Pt ratio in the same manner as does the isomerization rate (compare Figs. 2 and 3). The fact that the former is proportional to the 1-pentene concentration, and that little hydrogenation of *cis*-2-pentene occurs, suggests that perhaps for steric reasons the 2-pentyl radical cannot be cleaved from the platinum atom although it may isomerize. We therefore envisage the following scheme, the radicals being understood to be attached to platinum atoms:

$$\begin{tikzcd}
\text{1-pentene} \arrow[r, shift left] \arrow[dr, leftrightarrow] & \text{1-pentyl} \arrow[l, shift left] \arrow[r] & n\text{-pentane} \\
cis\text{-2-pentene} \arrow[r, shift left] & \text{2-pentyl} \arrow[l, shift left] \arrow[r, shift left] & trans\text{-2-pentene} \arrow[l, shift left]
\end{tikzcd}$$

The reactivity of styrene is consistent with the view that only 1-alkyl radicals may be hydrogenated, for on steric grounds styrene is more likely to yield the 2-phenylethyl radical than the 1-phenylethyl radical.

The reversibility of ethyl radicals formed from ethylene could be demonstrated by suitable isotopic tracer experiments.

We now try to explain the high *trans*-isomer yield. In this and related systems otherwise catalyzed (*8*), it is usually between 60% and 70%, but sometimes less that 50% (*9*); with the platinum(II)–tin(II) catalyst it never falls below the equilibrium 82% (*10*) and is usually much higher. The stereochemical determining step is (2′) and its course is determined by the conformation of the coordinated 2-pentyl radical in the transition state. If we assume the transition state to be planar (C, C, H, Pt), then there are two possible conformations (see Fig. 4): from A ("fully eclipsed") only the *cis* isomer can form and from ("eclipsed") B only the *trans*. If we ignore the constant interactions between the CH_3 and C_2H_5 groups with the Pt atom and the other ligands, the relative stabilities of A and B are determined by the repulsions between the nonbonded H atoms. Pitzer (*11*) has calculated for *n*-butane that the "eclipsed" and "fully eclipsed" conformations lie, respectively, about 3 and 4 kcal mole^{-1} above that for the most stable, "staggered" conformation; if the energy difference between conformers A and B is 1 kcal mole^{-1}, the *trans*-isomer yield will be 84.6% at 20°C, in very good agreement with our results. However, recent calculations by Scott and Scheraga (*12*) suggest that these conformations lie about 3 and 10.5 kcal mole^{-1} above that of the "staggered" conformation; this would mean virtually 100% *trans*-isomer yield. If this very high energy for the "fully eclipsed" conformer is valid, it may be that the transition state for formation of the *trans* isomer is not strictly planar but that reaction most often occurs when its orientation is such that the energy difference between it and the transition state for forming the *cis* isomer is about 1 kcal mole^{-1}. The observed activation energy difference for forming the two isomers (1.4 ± 0.2 kcal mole^{-1}) supports this idea.

Cramer and Lindsey (*9*) have recently reported a brief study of the reaction of 1-butene in CH_3OD with the Pt-Sn catalyst, but the Pt/Sn ratio used is not mentioned. Considerable amounts of 1-butene-d_1 were formed, and some 55% of the 2-butenes formed contained no D atoms. Unfortunately no analysis of the butane was made, and no experiments were performed using D_2 in place of H_2. Although the *trans*-isomer yields were high (72–77%), they were less than the equilibrium yield at the same temperature. These authors do not emphasize that isomerization only occurs in the presence of hydrogen, and their results are readily explained if the rate of the reaction

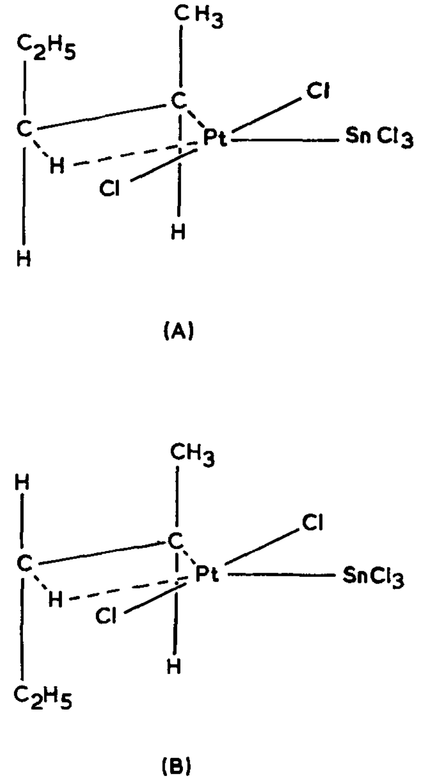

FIG. 4. "Eclipsed" conformations of a 2-pentyl radical coordinated to Pt: planar transition complex.

$$Pt\text{—}H + CH_3OD \rightarrow Pt\text{—}D + CH_3OH$$

is comparable with that of the analog of step (2).

The possibility that isomerization occurs by an olefin–π-allyl interconversion needs to be considered. However, if the H atom released in forming the π-allyl radical from the olefin were bonded to the platinum, two coordination sites would have to be generated (coordinated π-allyl radical occupying two) and this would mean the loss of one or two further ligands depending on whether or not the platinum became five coordinate. We consider this mechanism unlikely; furthermore, if it operated we should expect to see isomerization occurring in the absence of hydrogen. It does not.

One other system is known in which isomerization of a terminal olefin leads chiefly to a *trans* isomer. The isomerization of 4-methyl-1-pentene during its hydroformylation with $HCo(CO)_4$ as catalyst yields first 4-methyl-2-pentene (87.2% *trans*) before forming 2-methyl-2-pentene (*13*). Similarly the isomerization of 1-pentene catalyzed by $HCo(CO)_4$ under nitrogen gives 84.5% *trans*-2-pentene (*14*). We propose that the mechanisms and stereochemistry of these reactions are similar to that discussed above.

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