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Homogeneous Catalysis by Noble Metal Salts

I. The Homogeneous Isomerization of Olefins by Palladium Compounds

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Isomerization of the *n*-pentenes in benzene solution is catalyzed by palladous chloride and its nitrile complexes, and proceeds smoothly at 70°C and atmospheric pressure; ethyl acetate and methyl ethyl ketone are also suitable as solvents. The reactions proceed very much more slowly at 40°C in the absence of solvents. *cis*-2-Pentene isomerizes more slowly than does 1-pentene under equivalent conditions, and always exhibits an induction period. The ratio of *cis*-2-pentene/*trans*-2-pentene formed initially from 1-pentene exceeds the equilibrium ratio. Possible mechanisms are briefly discussed.

INTRODUCTION

The feasibility has recently been revealed of isomerizing olefins homogeneously under mild conditions with catalytic quantities of palladous chloride or its *bis*(benzonitrile) or ethylene complex (*1–4*). For example, on refluxing 4-methyl-1-pentene with palladous chloride (4×10^{-2} molar %) at 65°C, the equilibrium distribution of isomers was attained in 1 hr (*1*). 1-Hexene isomerized less rapidly and its presence inhibited the isomerization of branched olefins (*2*). π-Allyl palladous chloride was not an effective catalyst and the reaction was supposed not to proceed through a π-allylic intermediate (*1*). Davies (*3*) has reported a brief study under conditions such that double-bond migration past a methyl branch does not occur.

The possible causal connections between homogeneously and heterogeneously catalyzed reactions is now beginning to be appreciated and we have therefore further examined olefin isomerization in view of its relevance to the known high tendency of solid palladium catalysts to isomerize olefins during their hydrogenation (*5*). Isomerization of the pentene isomers was selected for study in view of the ease of analysis.

EXPERIMENTAL

Reactions were performed in a 20 ml round-bottomed vessel fitted with a condenser and a short sidearm sealed with serum cap. The reactants were charged into the vessel which was then placed in a water bath at the desired temperature, and timing was started at the onset of vigorous refluxing. Small samples were extracted through the serum cap with a hypodermic syringe at suitable intervals and analyzed by gas–liquid chromatography using silver nitrate in benzyl cyanide as the stationary phase at room temperature. No particular precautions were taken to dry the apparatus or reactants.

RESULTS

Preliminary experiments employed 10 ml of either 1-pentene (98.5%) or *cis*-2-pentene (93.5%) and 0.2 or 0.4 g of either palladous chloride or its bis(benzonitrile) complex (*6*) or its bis(acetonitrile) complex (prepared analogously), at about 40°C. The catalysts did not dissolve completely, and only very slow rates of isomerization were obtained (see Figs. 1 and 2). A saturated solution of

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the bis(benzonitrile) complex in 1-pentene was about $2 \times 10^{-3}\,M$ at this temperature, and that the reaction was partly heterogeneous was demonstrated by the increase in rate which resulted on agitating the system with a magnetically operated stirrer. Approximately equal rates were given by equal *weights* of the three catalytic species employed. Much trouble was also experienced with loss of olefin by evaporation, which accounts for the apparent acceleration seen in Fig. 1.

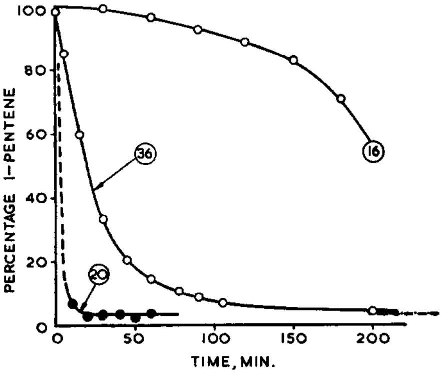


FIG. 1. The isomerization of 1-pentene. Run 16: no solvent, 40°C; 0.4 g $PdCl_2$ (equivalent to 0.22 *M* if dissolved completely). Run 20: 20% vol/vol 1-pentene in C_6H_6, 70°C; 0.2 g $PdCl_2$. Run 36: 20% vol/vol 1-pentene in C_6H_6 at 70°C; 0.02 g $PdCl_2 \cdot 2C_6H_5CN$ ($5.2 \times 10^{-3}\,M$).

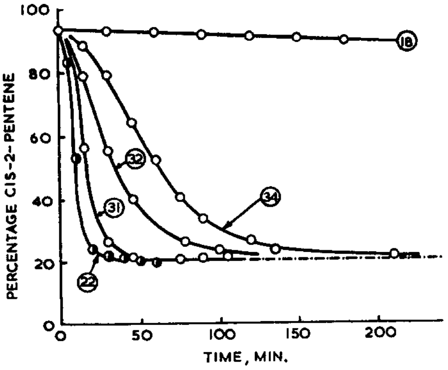


FIG. 2. The isomerization of *cis*-2-pentene. Run 18: no solvent, 40°C; 0.4 g $PdCl_2$. Run 22: 20% vol/vol pentene in C_6H_6, 70°C; 0.1 g $PdCl_2$. Run 31: 20% vol/vol pentene in C_6H_6, 70°C; 0.04 g. $PdCl_2 \cdot 2CH_3CN$ (0.0154 *M*). Run 32: 20% vol/vol pentene in C_6H_6, 70°C; 0.02 g $PdCl_2 \cdot 2C_6H_5CN$ ($5.2 \times 10^{-3}\,M$). Run 34: 20% vol/vol pentene in C_6H_6, 70°C; 0.02 g $PdCl_2$ (0.011 *M*).

However, on using the olefin (20% vol/vol) in benzene solution at about 70°C, very much faster rates of isomerization were observed with only 20 mg of the nitrile complexes which were now completely soluble ($PdCl_2 \cdot 2C_6H_5CN$, $5 \times 10^{-3}\,M$, molar olefin/catalyst ratio 500; $PdCl_2 \cdot 2CH_3CN$, $8 \times 10^{-3}\,M$, molar olefin/catalyst ratio 300). These and other results are also shown in Figs. 1 and 2. Palladous chloride was also more soluble under these conditions, and gave faster rates than before (see also Figs. 1 and 2).

The isomerization of *cis*-2-pentene invariably showed an initial acceleration in rate: by extrapolation an "induction period" of 1.5 to 13 min was estimated, and this varied approximately as the reciprocal of the molar catalyst concentration for either palladous chloride or the nitrile complexes, but was some six times longer at equivalent concentrations in the case of the former (see Fig. 3). Induction periods have been observed previously when palladous chloride was used as catalyst (*1*). We have observed no such phenomenon with 1-pentene. No induction period was apparent in an experiment where the reactant olefin had the composition: 5.5% 1-pentene, 87.5% *cis*-2-pentene, and 7% *trans*-2-pentene. For *cis*-2-pentene isomerization, the maximum rate is approximately proportional to the quantity of palladous chloride taken (compare Runs 22 and 34): 1-pentene isomerizes some 40% faster than *cis*-2-pentene with this cata-

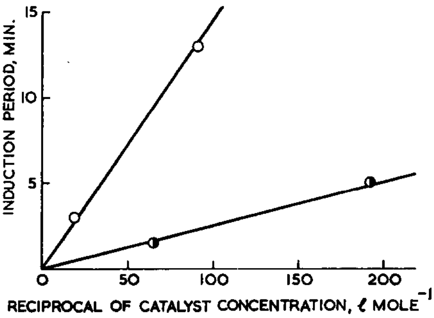


FIG. 3. Variation in the induction period observed in the isomerization of *cis*-2-pentene in benzene with catalyst dilution (liter mole^{-1}): open points, $PdCl_2$; half-filled points, $PdCl_2 \cdot 2C_6H_5CN$.

lyst. In each reaction, the nitrile complexes (which are equally reactive) are some three to four times more effective than palladous chloride on an equimolar basis. On the assumption that the rate is proportional to the concentration of $PdCl_2{\cdot}2C_6H_5CN$ in solution at both temperatures, we estimate that increasing the temperature from 40° to 70°C increases the rate of 1-pentene isomerization by a factor of about 100 (E = 25 kcal mole^{-1}) and the rate of *cis*-2-pentene isomerization by a factor of about 250 (E = 45 kcal mole^{-1}).

Two full courses of reaction are shown in Figs. 4 and 5. The initial ratio of *trans*-2-pentene/*cis*-2-pentene formed from 1-pentene is considerably less than the equilibrium ratio (Fig. 4), and the concentration of *cis*-2-pentene passes through a maximum (25–27%) before declining towards its equilibrium concentration. This behavior, which was generally observed, emphasizes that the initial *trans*/*cis* ratio is controlled by kinetic rather than thermodynamic factors. The 1-pentene formed from *cis*-2-pentene attains its equilibrium concentration very much earlier than the *cis* and *trans* isomers attain theirs, and it appears that the rate of *cis*–*trans* isomerization only reaches a maximum when the 1-pentene reaches its maximum concentration. This is in accord with the observation (see above) that the addition of about 5% of 1-pentene to *cis*-2-pentene removes the induction period. Our results hint at the possibility that 1-pentene formed from *cis*-2-pentene slightly exceeds its equilibrium concentration (by 0.5–1.0%) before attaining it, but the effect is barely greater than the analytical uncertainty.

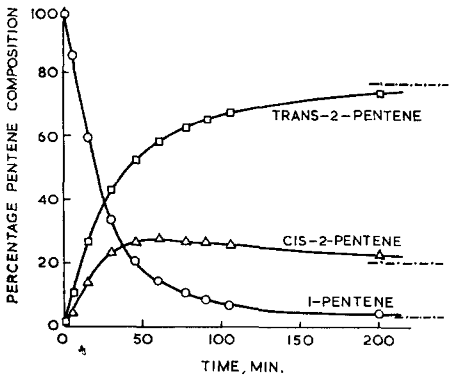


FIG. 4. The course of the isomerization of 1-pentene in Run 36 (see legend to Fig. 1 for conditions).

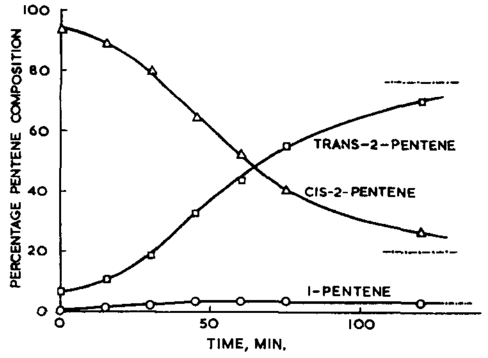


FIG. 5. The course of the isomerization of *cis*-2-pentene in Run 34 (for conditions see legend to Fig. 2).

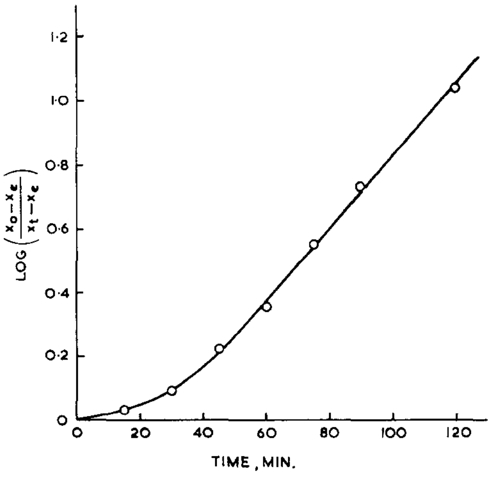


FIG. 6. First-order plot for the isomerization of *cis*-2-pentene in benzene solution at 70°C: palladous chloride concentration, 0.011 M.

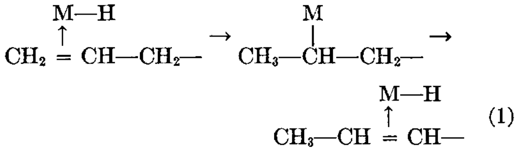
Figure 6 shows the first-order plot corresponding to Fig. 5 (x being the concentration of reactant olefin): The reaction of *cis*-2-pentene is first order in its concentration in excess of equilibrium, after the "induction period." Similar plots for reactions of 1-pentene show distinct decreases in slope in the latter stages, for reasons which are not understood. The following values for equilibrium concentrations of the isomers at 70°C, based on a number of measurements, were used in constructing first order plots: 1-pentene, 3.3 ± 0.5%; *trans*-2-pentene, 76.5 ± 0.5%; *cis*-2-pentene, 20.2 ± 0.5%.

Several other solvents besides benzene were tried. The nitrile complexes rapidly decomposed with deposition of metal on boiling their solutions in the lower alcohols (*4*); they were incompletely dissolved by cyclohexane and carbon tetrachloride. However they were soluble and stable in ethyl acetate and in methyl ethyl ketone, and successful runs were performed at 65°C with both these solvents; rates of *cis*-2-pentene isomerization were about the same as those obtained in benzene solution at 70°C.

No double-bond migration in 1,4-pentadiene could be detected under conditions where 1-pentene isomerized rapidly.

Discussion

Previous attempts (*3*, *4*) to discuss the mechanism of this reaction have not been eminently satisfactory. Harrod and Chalk (*4*) favor a mechanism which may be formalized as



$$CH_2 \overset{\overset{M-H}{\uparrow}}{=} CH-CH_2- \rightarrow CH_3-\overset{\overset{M}{|}}{C}H-CH_2- \rightarrow CH_3-CH \overset{\overset{M-H}{\uparrow}}{=} CH- \qquad (1)$$

The fact that no compound containing a Pd–H bond seems to have been isolated is not an insuperable objection, since such a compound may be sufficiently stable in solution to act as a catalytic species. These authors do not consider the possibility that such a species could arise by H abstraction from coordinated olefin with the formation of a π-allylic complex, and instead favor a mechanism in which a hydride ion is liberated from a carbanion formed by the nucleophilic attack of Cl^- on coordinated olefin. The full implications of this proposal are not developed.

Our experiments using solvents were performed at a temperature (70°C) where the formation of a π-allylic complex is possible (*7*) by the process

$$[(C_5H_{10})PdCl_2]_2 \rightarrow [(\pi\text{-}C_5H_9)PdCl]_2 + 2HCl \qquad (2)$$

It is evident that double-bond migration could occur by this reaction and its reverse, providing the hydrogen returned to a carbon atom other than that which it left. Under Davies' conditions however this seems not to occur (*3*). The observation that π-allyl palladous chloride is not itself a catalyst is not a valid objection to a π-allylic mechanism since the former may be more stable than a π-pentenyl complex and thus the catalyst site may be virtually "poisoned." There is a dearth of information on the stability of π-allyl complexes.

The apparent activation energies are improbably large for a catalyzed reaction, and it is plausible to argue that our results suggest a change in mechanism, and that they confirm the importance of π-allylic intermediates which are known not to be formed below 50–60°C (*7*).

Another possible mechanism of isomerization is represented by the process

$$[(C_5H_{10})PdCl_2]_2 \rightarrow (\pi\text{-}C_5H_9)PdCl_2 + (C_5H_{10})PdHCl_2 \qquad (3)$$

The plausibility of the hydridic species has been commented on above. Isomerization could occur by the reversal of this process, or alternatively the hydridic species could participate in mechanism (*1*).

The preferred formation of the less stable *cis* isomer on isomerization of a terminal olefin is a phenomenon of wide occurrence. It has been detected when using ethylene platinous chloride and rhodium trichloride homogeneously (*4*), Group VIII metal-supported catalysts (*5*), silica-alumina and silicotungstic acid (*8*), α-titanous chloride (*9*), and acid-base catalysts, especially lithium 2-aminoethylamide in ethylenediamine (*10*); we must presume its generality to betoken a root cause. Which isomer is formed is governed by the orientation of the bond between carbon atoms 3 and 4 at the time of formation of the allylic species (if such is indeed formed), which is then frozen in either a *syn* or an *anti* configuration. The addition of an hydrogen atom to carbon atom 1 will then yield either a *cis*-2-olefin from the *anti*- or a *trans*-2-olefin from the *syn* configuration [we use these terms in the current illogical manner (*11*)]. The preferred formation of the *cis* isomer can therefore be attributed to a preference for a π-allylic radical or some related species to exist in the more compact *syn* configuration or conformation. A similar argument based on the known stabilities of isomeric π-olefin complexes has been advanced by Harrod and Chalk (*4*).

The π-allylic mechanism outlined above cannot account for the direct interconversion of a *cis* isomer to a *trans* isomer or vice versa. Cis–trans isomerization could occur through the sequence:

$$cis\text{-2-pentene} \rightleftarrows \text{1-pentene} \rightarrow trans\text{-2-pentene}$$

or alternatively by migration of the double bond from C-2–C-3 to C-3–C-4. In this latter case, the resulting isomer would be determined only by the instantaneous orientation of the C-4–C-5 bond, and the chance of isomerization in each migration would hence be close to 50%. The possibilities are not readily distinguished between in our system, but two observations suggest the mechanism involving 1-pentene to be correct. (a) The rate of isomerization of *cis*-2-pentene is slower than that of 1-pentene under equivalent conditions, and (b) its rate only rises to a maximum after an induction period during which 1-pentene achieves its equilibrium concentration. The removal of the induction period by initially added 1-pentene suggests strongly that it acts catalytically in *cis–trans* isomerization.

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