

Catalysis

CALORIMETRIC INVESTIGATION OF PALLADIUM-CATALYSED TELOMERIZATION OF ISOPRENE IN SOLUTION

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Telomerization of isoprene is characterized by intense thermal effects. The reaction system di- μ -chlorobis(η^3 -allyl)-dipalladium(II): tri-*n*-butylphosphine: sodium methylate: isoprene = 1:2:3:200 in a solvent-mixture of methanol:benzene = 1:3 is used as a model. It is concluded that reaction of the catalyst combined with reduction of Pd(II) is followed by the telomerization reaction. There is a marked influence of Pd and phosphine concentration in the catalyst as well as concentration of isoprene. Results are available to optimize technical applications.

Keywords: isoprene, telomerization reaction

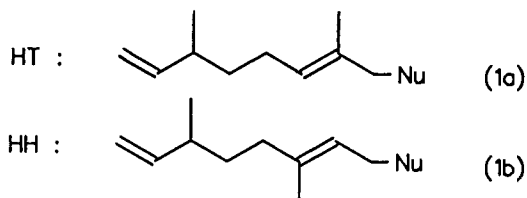
Introduction

Telomerization corresponds to dimerization with simultaneous addition of a nucleophile. In the last two decades the telomerization of 1,3-dienes by complex catalysis in homogeneous solution has been investigated repeatedly [1-7].

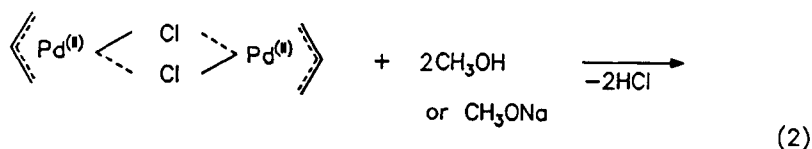
For telomeres of isoprene (2-methylbuta-1,3-diene) one obtains, depending on the kind of nucleophile selected (water, methanol, ammonia, acetone), valuable chemical perfumery products as well as intermediate products for the processing industry.

In this way W. Hoffmann in 1971 [1] prepared 3,7-dimethyl-octa-1,6-dienyl-ether using a palladium catalyst very selectively. Usually these reactions lead to regio-isomers, which are characterized by so-called head-head (HH) and head-tail (HT) structures:

Because the native terpenes possess an asymmetrical structure with HT connection, the HT products are of great practical interest, for instance as analogues of geraniol, nerol, citronellol and linalol.



We chose an investigation model consisting of Pd:tri-*n*-butylphosphine (Bu₃P):sodium methoxide (CH₃ONa):isoprene (IP) in the proportions 1:2:3:200. The reaction was studied in a mixed solvent of methanol and benzene. The starting material selected for the catalyst was di- μ -chlorobis (η^3 -allyl)-dipalladium(II), which was reduced in solution by sodium methoxide to Pd(0).



To prevent coagulation of metallic palladium immediately after the reduction represented by equation 2 we kept Pd(0) in stable solution by a ligand (*L*). Satisfactory complex formation is guaranteed by tri-*n*-butylphosphine, following which the catalytic cycles of the catalyst species L_{*n*}Pd(0) can occur. With a substrate of 1,3-dienes this catalyst forms octadienyl-palladium complexes.

The probable mechanism of the reaction was proposed by Hughes and Powell [8]. The reaction products are formed by hydrogen transfer from CH₃OH to the C-atom in position 6 and subsequent reductive elimination. In the present case two main products were obtained according to Eq. 1a and 1b with Nu = -OCH₃.

HT : 8-methoxy-3,7-dimethyl-octa-1,6-diene (Eq. 1b);

HH : 8-methoxy-3,6-dimethyl-octa-1,6-diene (Eq. 1a).

Experimental conditions

The complex compound of Pd(II) represented in Eq.(2) was weighed in the solid state and added to a mixed solvent of methanol and benzene under argon. Bu₃P was then added immediately followed by isoprene. After complete dissolution of all components the mixture was transferred, again under argon, to the reaction chamber of the calorimeter.

The reductive component CH₃ONa for the formation of the catalyst was kept near the reaction chamber in the thermostat of the calorimeter. The reaction was

started by injection of the methoxide. As a result, the stabilized Pd(0)-catalyst was formed and the telomerization of isoprene began. After the reaction had ended (5–50 hours), the mixture of products was analysed quantitatively by GC. Thus the degree of conversion and the product distribution between HT and HH structures were determined.

Calorimetric investigations of the reaction were carried out in two different calorimeters suitable for long-duration measurements under anaerobic conditions. The first was an isoperibolic calorimeter with a 60 ml Dewar bottle as reactor [9]. The second was a twin-type calorimeter [10] in a precision thermostat ($\pm 2 \cdot 10^{-4}$ K). Both calorimeters were fully computer-aided and allowed on-line description of the reaction as well as a calibration which was adjusted to the thermodynamic and kinetic evaluation of the data. Using the Tian equation the kinetic parameters were calculated automatically.

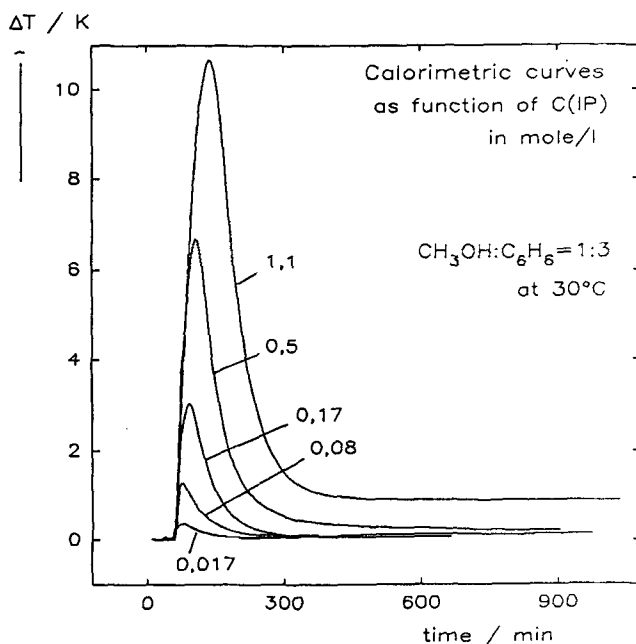


Fig. 1a Calorimetric curves as function of C(IP) in mol/l. $\text{CH}_3\text{OH}:\text{C}_6\text{H}_6 = 1:3$ at 30°C

Results for the solvent mixture methanol:benzene 1:3

In preparative work prior to our calorimetric measurements, N. Heldt used a standard reaction mixture: $\text{C(IP)} = 2.0$; $\text{C(Pd)} = 10^{-2}$; $\text{C(Bu}_3\text{P)} = 2 \cdot 10^{-2}$ and

$C(\text{CH}_3\text{ONa}) = 3 \cdot 10^{-2}$ mole per liter at 30°C . In the following account the proportions have been changed systematically.

Dependence on isoprene concentration

Figures 1a and b show the calorimetric curves, temperature differences ΔT against time t , under standard conditions as a function of $C(\text{IP})$ in mol per l. The experiment with 2.0 mol/l occupies an intermediate position. While at higher concentrations a clear differentiation between two steps of reactions is possible, these steps amalgamate to form one peak below concentrations of 2 mol/l. These two stages of reaction correspond, on the one hand, to formation of the Pd-catalyst (reduction by CH_3ONa) and on the other to the increasing exothermic reaction of telomerization. Figure 1b shows that the reaction with 4.1 mol/l requires about 14 h for completion.

Figure 2 shows the relationship between heat production and the amount of the isoprene input. The resulting straight line signifies one main reaction. It should be mentioned that the heat of reaction for reduction of Pd in the absence of isoprene amounts to 0.278 kJ if the standard input $C_{\text{rel}} = 1.0$ is used, i.e. the ΔH value has to be lowered accordingly.

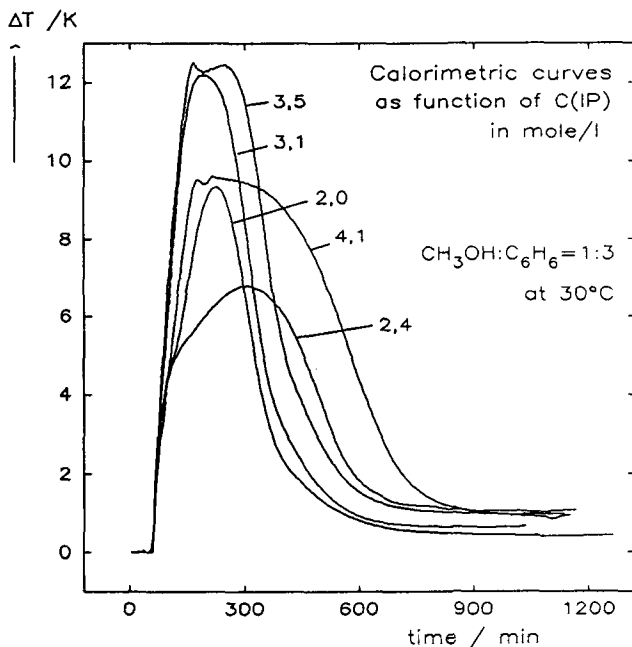


Fig. 1b Calorimetric curves as function of $C(\text{IP})$ in mol/l. $\text{CH}_3\text{OH}:\text{C}_6\text{H}_6 = 1:3$ at 30°C

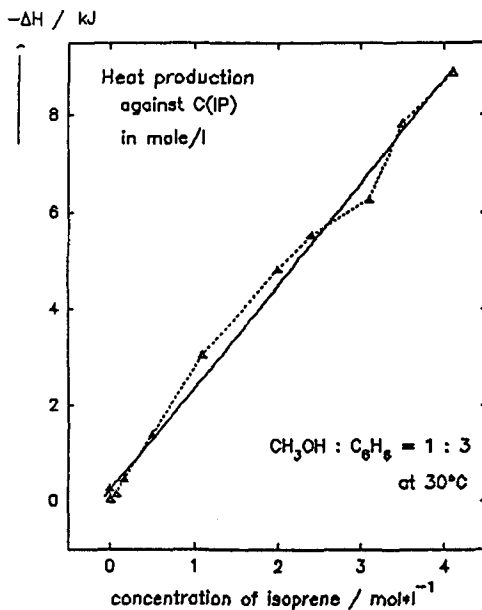


Fig. 2 Heat production against C(IP) in mol/l. $\text{CH}_3\text{OH}:\text{C}_6\text{H}_6 = 1:3$ at 30°C

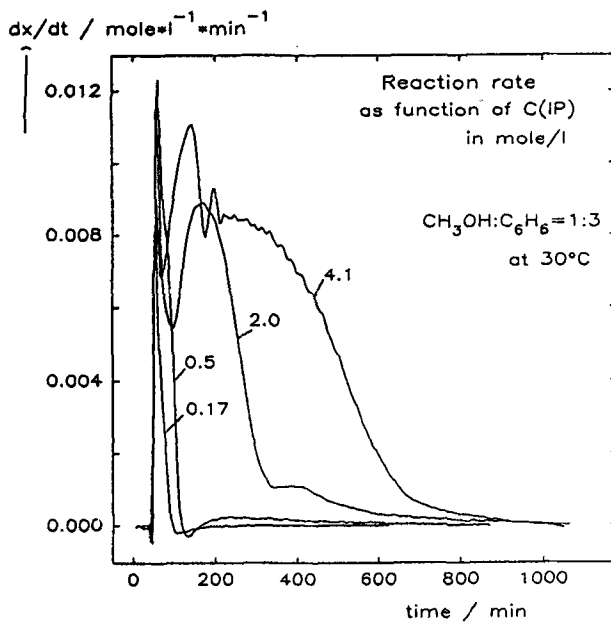


Fig. 3 Reaction rate as function of C(IP) in mol/l. $\text{CH}_3\text{OH}:\text{C}_6\text{H}_6 = 1:3$ at 30°C

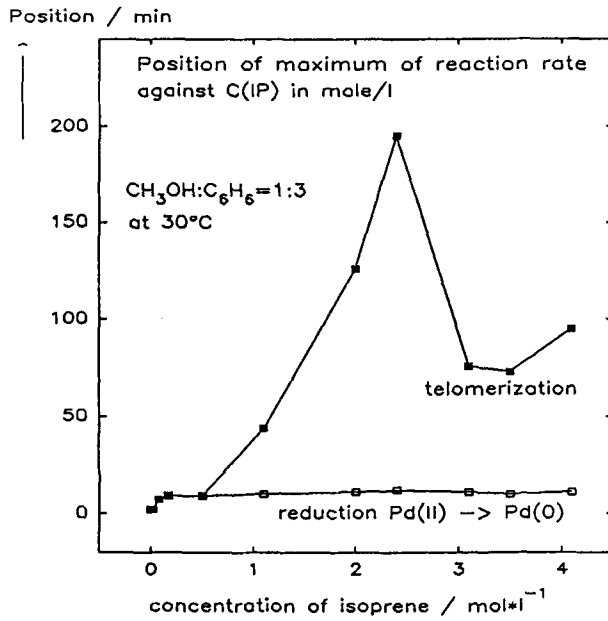


Fig. 4 Position of maximum of reaction rate against C(IP) in mol/l, CH₃OH:C₆H₆ = 1:3 at 30°C

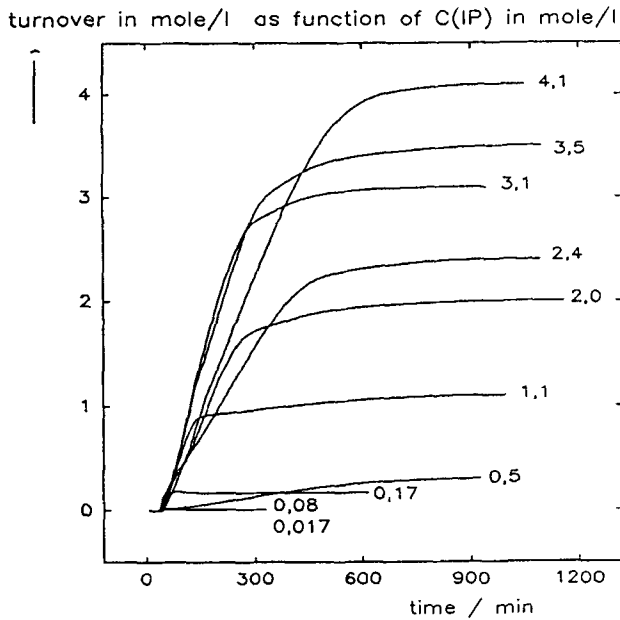


Fig. 5 Turnover as function of time for isoprene

Figure 3 shows the course of the rate of reaction dx/dt after evaluation of the experimental curves according to the equation of Borchardt and Daniels [11]. Above 0.5 mol/l isoprene, splitting into Pd-reduction and telomerization is clearly visible. Above 2 mol/l a third reaction becomes apparent.

If one compares the positions of the maxima of the reaction rate RR on the time axis as a function of $C(\text{IP})$ in Fig. 4, two facts become evident. The course of formation of the Pd catalyst is identical in all experiments, while the RR maxima of telomerization have a retardation of 10 to 200 minutes. With increasing $C(\text{IP})$ these values decrease. This can be explained as follows. The initial rise reflects the well-known substrate inhibition. Release of the newly-formed telomeres from the catalyst is the rate-determining step and leads to inhibition of catalysis. If there is much isoprene, the separation process is supported by an increasing displacement reaction; thereby the telomerization process is accelerated.

Figure 5 shows the turnover in mole per liter as a function of time for different initial amounts of isoprene. It can be seen that for up to 3.5 mol/l isoprene a fast and effective turnover is possible with the help of the catalyst used.

The ratio of the regio-isomers HT/HH has a constant value of 3.5, if $C(\text{IP})$ exceeds 2.0. This means that with increasing IP input the same products but with a relatively high HT portion will be formed.

Catalysis dependence on palladium concentration

If the catalyst is not prepared in the ratio $1\text{Pd} : 2\text{Bu}_3\text{P} : 3\text{CH}_3\text{ONa}$ but with a lower portion of palladium, then the calorimetrically obtained results for $C(\text{IP}) = 2.0$ mol/l are as follows. The present investigations have demonstrated that a high degree of conversion can be achieved with a relatively small portion of palladium in the standard mixture. Integration of the experimental curves yields the calculated turnover curves which are shown in Fig. 6 for various Pd inputs. A remarkably high increase in the conversion from $C_{\text{rel}} 0.2$ to 0.3 was found; for the latter value a conversion of 100% was achieved. From this it can be concluded that between 0.3 to 1.0 a high reserve of catalyst capacity exists. Above $C_{\text{rel}} = 0.5$ the course-of-time curves are so similar that reduction of the Pd input appears possible.

Dependence on the amount of phosphine as ligand of palladium

In the next step the portion of Bu_3P was changed while the standard catalyst remained in the constant ratio Pd to $\text{Bu}_3\text{P} = 1:2$. Figure 7 shows the calorimetric curves for increasing proportions of phosphine between 1:6 and 1:0.5. The corresponding conversion curves demonstrate that the ratios 1:1 to 1:4 lead to a complete turnover, but not at the same reaction rate. This indicates that too high a concentration of the complex ligand inhibits the effective course of catalytic telomerization, although the HT/HH-ratio can be raised further.

Formation of the tetrakis type of coordination of the phosphine at the Pd centres becomes so stable that the isoprene can no longer be coupled so favoura-

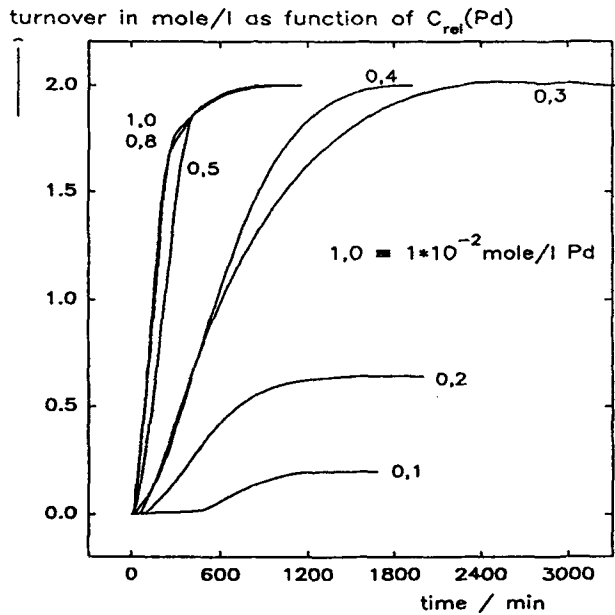


Fig. 6 Turnover as function of time for different Pd inputs

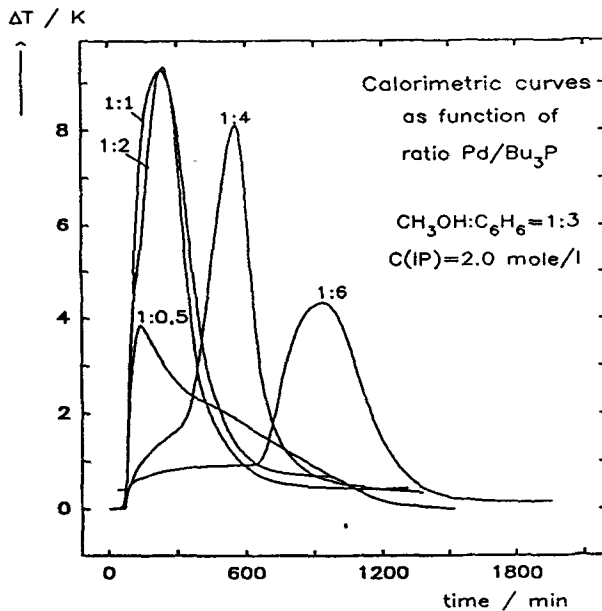


Fig. 7 Calorimetric curves as function of ratio Pd/Bu₃P. $CH_3OH:C_6H_6 = 1:3$ $C(IP) = 2.0$ mol/l

bly – i.e. the exchange will be markedly inhibited. On the other hand, stabilization of the Pd(0) at low phosphine concentrations is no longer sufficient. Under these conditions there is a third RR maximum due to the precipitation of metallic Pd.

Conclusions

The main results of our investigations are:

1. Calorimetry is a suitable method for investigating telomerization as a specific case of dimerization.
2. Processes under anaerobic conditions can be controlled for long periods of time.
3. Differentiation between formation of the catalyst, telomerization and precipitation of Pd leads to useful discussion of quantitative aspects.
4. Thermodynamic and kinetic parameters determined provide effective means for optimizing these important reactions.

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Zusammenfassung — Die Telomerisation von Isopren ist durch intensive thermische Effekte gekennzeichnet. Als Modell wurde das Reaktionssystem: Di- μ -Chlorobis(η -allyl)-dipalladium(II): Tri-*n*-butylphosphin: Natriummethylat: Isopren = 1:2:3:200 in einem Lösungsmittelgemisch von Methanol:Benzol = 1:3 benutzt. Es wird geschlossen, daß auf die mit der Reduktion von Pd(II) verbundene Reaktion des Katalysators die Telomerisationsreaktion folgt. Es besteht eine deutliche Abhängigkeit von der Pd- und Phosphinkonzentration im Katalysator und auch von der Isoprenkonzentration. Resultate zur Optimierung technischer Anwendungen sind verfügbar.