

Investigations of the progress of an organic chemical reaction by precision calorimetry. Part 2¹

H. Anderson * and N. Heldt

University of Greifswald, Department of Chemistry, Soldtmannstr. 16, D-2200 Greifswald (Germany)

(Received accepted 24 May 1993)

Abstract

The application of calorimetry to the dimerization of isoprene yielded various results that depend on the homogeneous palladium catalyst, its composition, the solvent selected and, not least, the concentration of isoprene. The influences of all the variables were optimized with respect to the turnover and the ratio of the two main products that are the head–head or head–tail configurations of dimeric isoprene. The products are of interest in perfumery.

INTRODUCTION

Telomerization is dimerization with simultaneous addition of a nucleophil. The telomerization of 1,3-dienes by complex catalysis in homogeneous solution has been attempted several times [1–4]. Telomers of isoprene (2-methylbuta-1,3-diene) yield, depending on the nucleophiles used (water, methanol, ammonia, acetone, etc.), valuable chemical products, for example in perfumery. In order to influence the telomerization reactions, various investigations into the mechanism of the complex-catalyzed diene reaction were made. Some basic mechanistic concepts were proposed by Wilke et al. [4, 5], Takahashi et al. [6, 7] and Hughes and Powell [8], and are described in ref. 9.

EXPERIMENTAL CONDITIONS

These investigations were performed in the same way as described in Part 1 of this work [9]. The same standard reaction mixture of di- μ -chlorobis(η^3 -allyl)-dipalladium(II)/tri-*n*-butylphosphan/sodium methylate/isoprene in a ratio of 1:2:3:200 was treated in a solvent mixture of

* Corresponding author.

¹ Presented at the Tenth Ulm Conference, Ulm, Germany, 17–19 March 1993.

methanol and benzene, the effects of other influencing factors also being considered. The main products were obtained: 8-methoxy-3,7-dimethyl-octa-1,6-diene (head/tail) and 8-methoxy-3,6-dimethyl-octa-1,6-diene (head/head).

From the calorimeter curves, the turnover and the reaction rate (see Part 1 [9]) can both be derived.

THE INFLUENCE OF P(III) LIGANDS

In the standard mixture given above, Bu_3P was applied as the stabilizing ligand. The influence on the reaction rate is clearly related to the ratio of P(III):Pd(II), the ratio 1:2 being particularly advantageous. At lower ratios, precipitation of metallic palladium was observed; higher ratios led to the formation of the tetrakis complex, causing a blockage of the Pd so that the turnover and the reaction rate was decreased [9].

The influence of various P(III) compounds on the telomerization was then analysed. The effect of these ligands can be explained with reference to their electronic and steric properties. The steric influences can be estimated after Tolman [10, 11] by a steric parameter θ_i . Ligands with higher space requirements are able to influence the process by coordinative addition of substrate only in a particular orientation or by blocking the coordinative sites, which leads the reaction in another direction. In addition, Tolman proposed an electronic parameter $\sum \chi_i$ for the basic character of the phosphorus ligands. To evaluate their influence on telomerization, the following phosphorus ligands were used in addition to Bu_3P : Et_3P , Pr_3P and cy_3P . The electronic and steric parameters of these ligands are shown in Table 1.

The phosphorus ligands have generally the same influence on the total yield. After completion of the reaction the turnover of the telomers was

TABLE 1

Steric and electronic parameters of the considered ligands

R	$\sum \chi_i$	θ_i	R	$\sum \chi_i$	θ_i
Et	5.6	132	Bu^n	4.2	139
Pr^i	3.1	160	cy	0.3	170

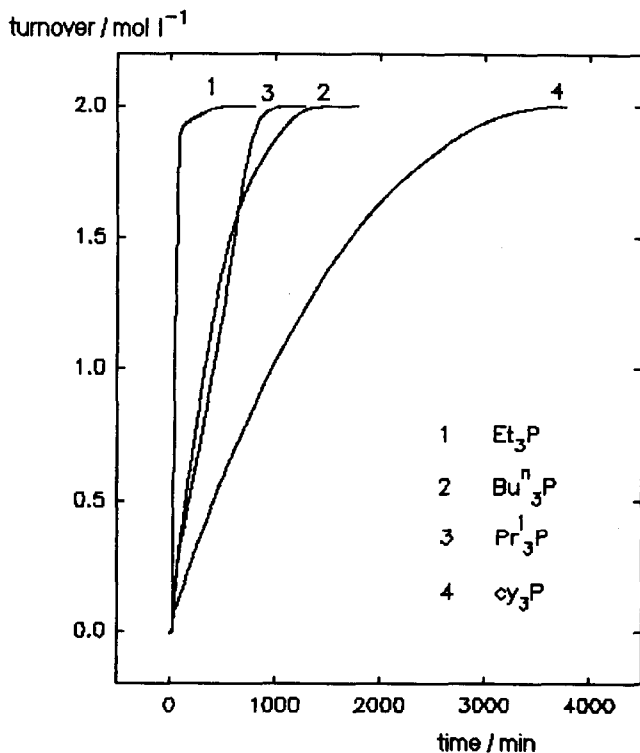


Fig. 1. Turnover curves for several P(III) ligands.

found to be 70–90%, with additional small amounts of dimers and methoxy-pentenes.

The influence of the applied phosphanes on the reaction rate is very important and is clearly related to their steric and electronic factors. Figure 1 shows that the reaction rate decreases with increasing steric and decreasing electronic factors.

THE EFFECT OF CHANGING THE RATIO OF METHANOL:BENZENE TO 3:1

In the standard mixture the solvent is present in a ratio of 1:3 [9]. From previous investigations [12, 13], it is known that an increasing portion of methanol in the solvent mixture leads to a lower reaction rate and at the same time the product ratio HT/HH is shifted in favour of head-head products. Therefore the influence of the isoprene concentration was investigated for a solvent mixture of 3:1. Our results demonstrate that the reaction enthalpies are not influenced by the choice of the solvent mixture

TABLE 2

HT/HH ratio and the reaction enthalpies at 30°C with varying isoprene concentrations

C(IP)/ mol l ⁻¹	HT/HH		ΔH /kJ	
	MeOH:C ₆ H ₆ = 1:3	MeOH:C ₆ H ₆ = 3:1	MeOH:C ₆ H ₆ = 1:3	MeOH:C ₆ H ₆ = 3:1
0.08	1.8	0.4	-0.16	-0.32
0.17	1.9	0.4	-0.46	-0.78
0.5	2.6	0.5	-1.39	-1.15
1.1	3.3	0.7	-3.04	-2.21
2.0	3.5	1.0	-4.81	-5.78
2.4	3.5	0.9	-5.53	-5.36
3.1	3.5	1.1	-6.73	-8.18
3.5	3.5	1.1	-7.83	-8.01

in contrast to the HT/HH ratio (Table 2). Consequently the calorimeter curves are essentially the same for both solvent ratios (Fig. 2).

From the curve of dx/dt plotted against time, it can be seen that the formation of the catalyst is not completed on the reduction of Pd. If the amount of catalyst is constant the slope of the dx/dt curve must decrease continually. Here the curves for more than 2.0 mol l⁻¹ isoprene show an inflection point. To build up the active species consisting of ligand, Pd(0) and solvent, a subsequent formation interval is necessary. It is obvious that

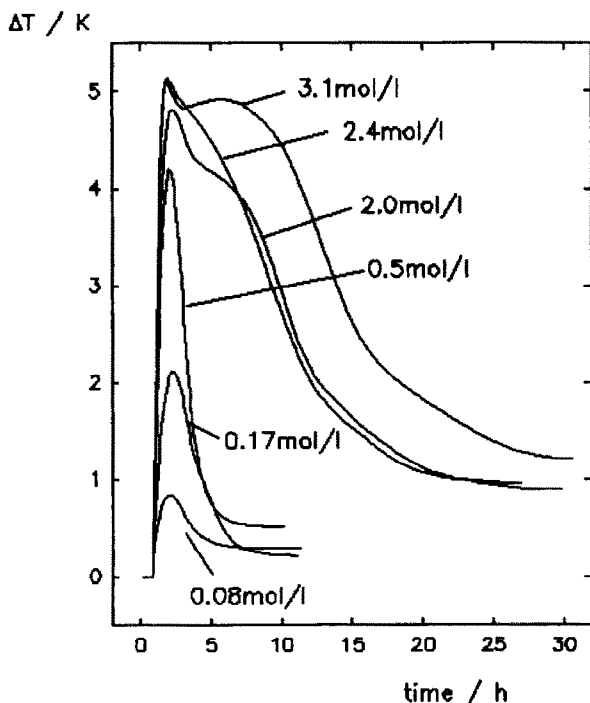


Fig. 2. ΔT - t curves for various isoprene concentrations.

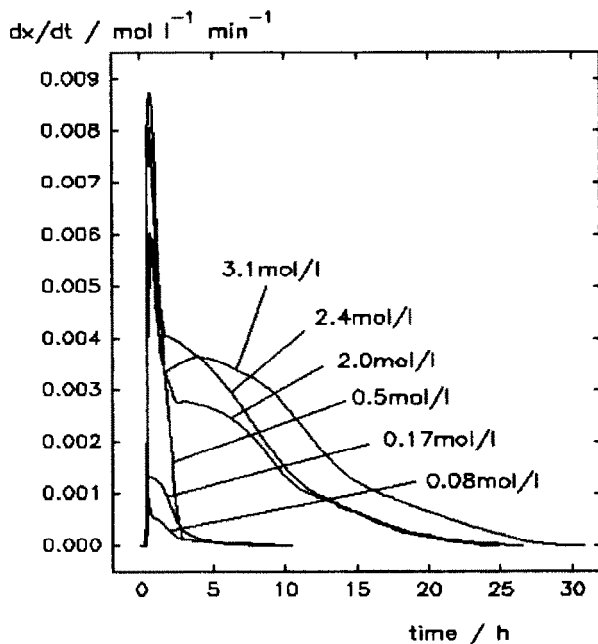


Fig. 3. Reaction rates as a function of time for various isoprene concentrations.

the isoprene is actively involved in these formation processes, as can be concluded from the evaluation of the curves in Fig. 3.

For low isoprene concentrations, the reduction of Pd, the formation of catalyst and the start of telomerization occur at the same time. This means that the active species of the catalyst becomes effective very rapidly. For higher isoprene concentrations, the rate of formation of the catalyst decreases so that the separation of the first maximum (reduction) (see Fig. 2) and the second maximum at the end of the formation interval becomes straightforward. In the region of the second maximum, there are two superimposed processes. The long periods with little change in reaction rate can be explained firstly by the continuous growth in the catalyst concentration and, secondly, by the decreasing concentration of isoprene because of the permanent turnover of telomerization. If the concentration of isoprene is very high, then this second maximum occurs at a later time and, simultaneously, the earlier shoulder becomes a plateau in the curve. In this region, catalyst formation and telomerization occur side by side. Therefore, the rate of turnover is nearly constant. After leaving this plateau, most of the turnover has been completed.

No definitive explanation of the underlying chemical processes or mechanisms involved can be given at present.

THE INFLUENCE OF THE POLARITY OF ADDITIONAL SOLVENT COMPONENTS

A comparison of the maximal reaction rates of telomerization shows that the values for a methanol:benzene ratio of 1:3 are distinctly higher than for a ratio of 3:1. Obviously, the polarity of benzene is responsible for such a change in the reaction rate. In general, components with high transition energy (E_{trs}) diminish the reaction rate. To demonstrate the validity of this thesis, benzene was substituted by a series of alcohols: ethanol ($E_{\text{trs}} = 217.29 \text{ kJ mol}^{-1}$), *n*-propanol ($E_{\text{trs}} = 212.27 \text{ kJ mol}^{-1}$) and *n*-butanol ($E_{\text{trs}} = 210.18 \text{ kJ mol}^{-1}$). The nucleophilic reaction in the telomerization of isoprene was clearly dominated by the methanol, from its E_{trs} value of $232.37 \text{ kJ mol}^{-1}$. However, the reaction rate increases with decreasing polarity of the additional solvent component. Because of the small differences in the E_{trs} values, the changes in the reaction rate for the three added alcohols are, as expected, rather small (Fig. 4). With increasing

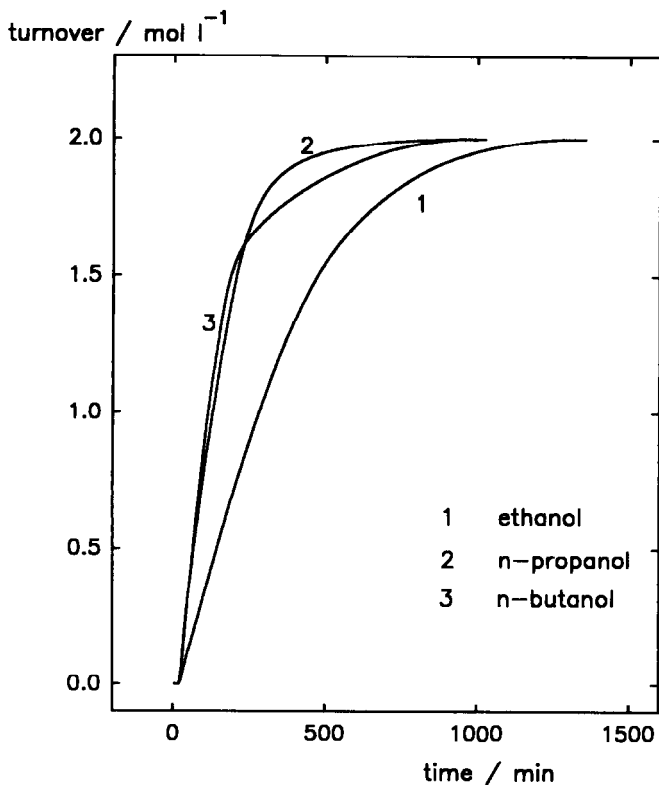


Fig. 4. Turnover curves for various alcohol-methanol mixtures (alcohol:methanol = 3:1).

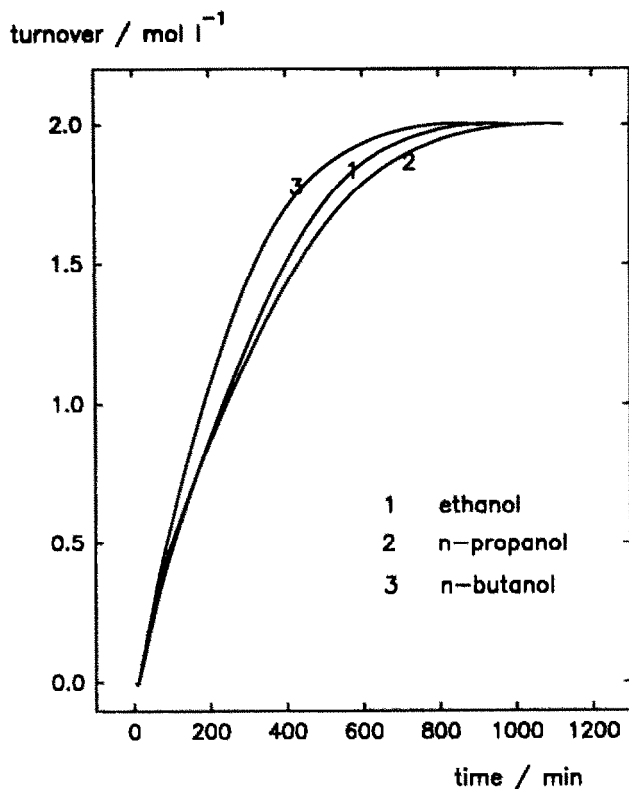


Fig. 5. Turnover curves for various alcohol-methanol mixtures (alcohol:methanol = 1:3).

amounts of methanol, the differences in the reaction rate becomes much smaller (Fig. 5).

DEPENDENCE ON TEMPERATURE

To determine the influence of temperature on the telomerization, the calorimetric investigations were extended to 25, 30, 35 and 40°C. Because the boiling point of pure isoprene is 34.1°C, it was not possible to work above 40°C. For the standard mixture, 40°C was the limit because ΔT -values in the calorimeter became very high. Only for the solvent mixture of ratio methanol:benzene = 3:1 could measurements be made at all four temperatures.

Figure 6 shows that the reaction becomes faster and faster as the temperature rises. No significant change in the reaction enthalpies is produced by varying the temperature from 25 to 40°C.

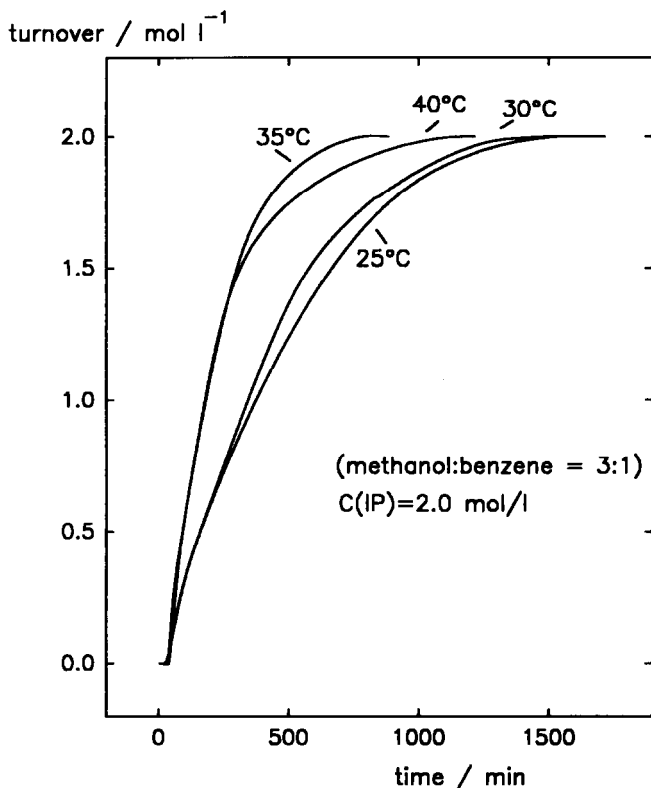


Fig. 6. Turnover curves at various temperatures.

REFERENCES

- 1 W. Hoffman, F.-J. Müller and K. von Fraunberg, BRD-OS 2 154 370.
- 2 J. Beger, Ch. Duschek and H. Reichel, J. Prakt. Chem., 315 (1973) 1077.
- 3 A. Behr and W. Keim, Chem. Ber., 116 (1983) 862.
- 4 G. Wilke, B. Bogdanovic, P. hardt, P. Heimbach, W. Keim, M. Kroner, W. Oberkirch, K. Tanaka, E. Steinruck, D. Walter and H. Zimmermann, Angew. Chem., 5 (1966) 151.
- 5 G. Wilke et al., Angew. Chem., 75 (1963) 10.
- 6 S. Takahashi, H. Yamazaki and N. Hagihara, Mem. Inst. Sci. Ind. Res. Osaka Univ., 25 (1968) 125.
- 7 Y. Takahashi, S. Sakai and Y. Ishil, J. Organomet. Chem., 16 (1969) 177.
- 8 R.P. Hughes and J. Powell, J. Am. Chem. Soc., 94 (1972) 7723.
- 9 N. Heldt, K. Heldt, H. Anderson and W. Gaube, Proc. 10th Int. Conf. Therm. Anal. Calorim. London, 1992, J. Therm. Anal., 40(3) (1993), in press.
- 10 C.A. Tolman, Chem. Rev., 77 (1977) 313.
- 11 C.A. Tolman, J. Am. Chem. Soc., 92 (1970) 2953.
- 12 H. Yagi, E. Tanaka, H. Ishiwatari, M. Hidai and Y. Ushida, Synthesis, (1977) 334.
- 13 K. Sawatari and E. Tanaka, Jap. Kokai 75 154 201 (CA 84,164122b).