PHOTO-ENHANCED CATALYSIS OF THE CYCLOTRIMERIZATION OF PHENYLACETYLENE BY THE NIOBIUM(V) CHLORIDE SYSTEM

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Summary

Niobium(V) chloride in a carbon tetrachloride solution catalyses the cyclotrimerization of phenylacetylene. The reaction is characterized by a well-defined induction period. During the induction period reduction of niobium(V) to catalytically active niobium(III) occurs. The reduction rate can be greatly accelerated by irradiating the system with visible light. The light effect is incorporated in a reaction scheme which makes it possible to describe the reaction course.

Introduction

Phenylacetylene is cyclotrimerized in the presence of niobium(V) chloride and tantalum(V) chloride to form 1,3,5- and 1,2,4-triphenylbenzene [1, 2]. The reaction course can be divided into three phases. Directly after mixing the reagents, a maximum of 2 mol phenylacetylene reacts with one mol niobium(V) chloride present in an equilibrium reaction. An induction period follows during which very little change can be detected but an active cyclization catalyst containing niobium(III) forms slowly, which leads to the cyclization reaction at the end of the induction period. The niobium(V) complex is spontaneously reduced by the phenylacetylene, but the abrupt termination of the induction period can only be explained by an autocatalytic step which accelerates the production of the niobium(III) catalyst [2].

The duration of the induction period, and thus the rate of formation of the initially formed niobium(III) species, is influenced by several factors such as the type of solvent, type of alkyne, alkyne concentration and temperature [3, 4]. If the solution is irradiated by visible light the induction period is also shortened.

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In this publication we wish to report on the effect of the irradiation on the induction period of the alkyne-niobium(V) chloride system.

Experimental

Solutions of niobium(V) chloride were prepared by saturating boiling carbon tetrachloride with niobium(V) chloride and thereafter cooling it to a predetermined temperature to obtain the necessary niobium(V) chloride concentration. The trimerization reaction of phenylacetylene was performed by injecting phenylacetylene directly into a specially made spectrophotometer cell. The cell, constructed from borosilicate glass with an optical path length of 0.8 mm, was fitted with a septum to introduce the reagents. Great care was taken to exclude oxygen and moisture by working in a dry nitrogen atmosphere. All reactions were performed at room temperature (295 K).

During the induction period the reaction mixture remains clear but darkens rapidly once the trimerization reaction commences, due to formation of black polymeric compounds as a byproduct. This general darkening was used to detect the transition of the induction period to the cyclization phase. The assembly illustrated in Fig. 1 was used to compare the darkening of an irradiated portion with the darkening of an unirradiated portion in the same sample.

A 250 M 24 V quartz halogen lamp (1) in combination with a high intensity monochromator was used to focus a beam of monochromatic light with a band width of 50 nm on a portion of the reaction mixture. The



Fig. 1. Irradiation assembly. 1 quartz halogen lamp, 2 Jarrel Ash high intensity monochromator, 3 reaction cell, 4 measuring light, 5 Zeiss M4Q monochromator, 6 photodiode, 7 photodiode, reference beam, 8 two-pen recorder.

transmittance at 900 nm of the irradiated and unirradiated portions of the sample were measured simultaneously by recording the output at the reference beam (7) and the irradiated portion (6) on a two pen recorder (8). A monochromator (5) was necessary to eliminate any effect of stray light on the output of the photodiodes. The weak light source of 0.5 W fitted with a red filter (4), which was used for the measuring beams, had no detectable photochemical effect on the reaction mixture, nor could any significant effect be found on the unirradiated portion as a result of stray light from the irradiating beam.

The light intensity of the irradiation beam was measured bolometrically to find the dependence of the light intensity on the wavelength and on the voltage on the quartz halogen lamp. By adjusting the voltage to the appropriate value, it was possible to change the light intensity at a fixed wavelength in a known manner, or to irradiate at constant intensities at different wavelengths. No attempt was made to measure absolute light intensities.

Results and discussion

General effect of irradiation

The shortening of the induction period by irradiating at 500 nm is illustrated in Fig. 2.

The termination of the induction period is found graphically as shown in Fig. 2. The induction period for the unirradiated sample is indicated by t_0 and t is used for the irradiated sample. The relative change in induction period as a result of irradiation is given by the ratio t/t_0 .



Fig. 2. The effect of irradiation on the induction period. $[NbCl_5] = 16 \times 10^{-3} \text{ mol dm}^{-3}$; $[C_6H_5C=CH] = 18.2 \times 10^{-3} \text{ mol dm}^{-3}$; $\lambda = 700 \text{ nm}$; curve 1 unirradiated portion, curve 2 irradiated portion.



Fig. 3. The effect of the irradiation wavelength on the induction period. $[NbCl_5] = 16 \times 10^{-3} \text{ mol dm}^{-3}$; $[C_6H_5C = CH] = 18.2 \times 10^{-3} \text{ mol dm}^{-3}$.

Wavelength dependence

The activation of the system is successful over the entire visible wavelength range, but notably less at wavelengths higher than about 600 nm, as can be seen in Fig. 3 at a constant irradiation level.

Light intensity

The influence of the irradiation level is shown in Fig. 4 for wavelengths of 700 nm and 500 nm.

Effect of the phenylacetylene concentration

The induction period is shortened by increasing the concentration of phenylacetylene for both the unirradiated and the irradiated samples, as shown in Fig. 5 for 500 nm irradiation.

The calculated curves in Figs. 4 and 5 were obtained by a numerical integration similar to that reported previously [2].

The rapid uptake of $C_6H_5C=CH$ by $NbCl_5$ directly after mixing is described by:

NbCl₅ + 2C₆H₅C=CH
$$\stackrel{k_1}{\underset{k_2}{\longleftarrow}}$$
 NbCl₃(C₆H₅C=CHCl)₂ (1)



Fig. 4. The effect of light intensity on the induction period. $[NbCl_5] = 16 \times 10^{-3} \text{ mol dm}^{-3}$; $[C_6H_5C==CH] = 18.2 \times 10^{-3} \text{ mol dm}^{-3}$; (\bullet) measured points for 700 nm irradiation; (\bigcirc) measured points for 500 nm irradiation; (--) calculated curves.

This equilibrium reaction has no effect on the duration of the induction period other than that the concentration of I is determined by the relative values of k_1 and k_2 . The reduction reactions (2) and (3):

$$NbCl_{3}(C_{6}H_{5}C = CHCl)_{2} + C_{6}H_{5}C = CH \xrightarrow{k_{3}} [NbCl_{3}] + oligomers$$
(2)

$$NbCl_{3}(C_{6}H_{5}C = CHCl)_{2} + [NbCl_{3}] + C_{6}H_{5}C = CH \xrightarrow{k_{4}} 2[NbCl_{3}] + oligomers$$
(3)

are mainly responsible for the termination of the induction period. It can safely be assumed that light activation occurs through a species which accelerates the formation of the catalytic $[NbCl_3]$ species, as the rate of the cyclotrimerization reaction (4)

$$3C_6H_5C = CH + [NbCl_3] \xrightarrow{k_5} [NbCl_3] + C_6H_3(C_6H_5)_3$$
(4)

has little effect on the induction period. Although it was not possible to obtain any of the individual rate constants, it was possible to compute a set of rate



Fig. 5. The effect of the phenylacetylene concentration on the induction period. $[NbCl_5] = 7.0 \times 10^{-3} \text{ mol dm}^{-3}$; 500 nm irradiation; (\bullet) measured induction period, unirradiated; (\bigcirc) measured induction period, irradiated; (---) calculated curves.

constants: $k_1 = 200$; $k_2 = 0.6$; $k_3 = 1 \times 10^{-4}$; $k_4 = 25$; $k_5 = 20$ by which the observed induction periods for the unirradiated sample at different phenyl-acetylene concentrations were correctly predicted (see Fig. 5).

The effect of irradiation was introduced by assuming the reaction

$$NbCl_3(C_6H_5C=CHCl)_2 \xrightarrow{k_6}{h_V} [NbCl_3]$$
 (5)

By taking $k_6 = (\text{light intensity})/20$ for 700 nm and $k_6 = (\text{light intensity})/2500$ for 500 nm, the calculated curves in Fig. 4 were obtained. The effect of light at different concentrations of phenylacetylene is also correctly described by taking $k_6 = 4 \times 10^{-4}$, as shown in Fig. 5. The photochemical reaction as given in reaction (5) was the only one in which we were able to match the observed induction period. Although it seems that photons of 500 nm are more than a thousand times more effective than photons at 700 nm in reducing the

intermediate $NbCl_3(C_6H_5C=CHCl)_2$, no such great differences in direct light absorption could be seen in the visible spectrum during the induction period.

We can conclude that the absorbed light energy facilitates the formation of the catalytically active niobium(III) species through a reductive elimination reaction of the initially formed $NbCl_3(C_6H_5C=CHCl)_2$ compound.

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References

- 1 T. Masuda, T. Mouri and T. Higashimura, Bull. Chem. Soc. Jpn., 53 (1980) 1152.
- 2 G. Lachmann, J. A. K. du Plessis and C. J. du Toit, J. Mol. Catal., 42 (1987) 151.
- 3 C. J. du Toit, J. A. K. du Plessis and G. Lachmann, S. Afr. J. Chem., 38 (1985) 8.
- 4 C. J. du Toit, J. A. K. du Plessis and G. Lachmann, S. Afr. J. Chem., 38 (1985) 188.