Pulse Radiolysis of Tetraphenylcyclobutane in Hexamethylphosphoric Triamide Solution

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r-1, c-2, t-3, t-4-tetraphenylcyclobutane (TPCB) was irradiated in dilute solutions of hexamethylphosphoric triamide (HMPT) with 20 ns pulses of 16 MeV electrons. Soltved electrons (e\textsubscript{solv}) produced during the radiolysis of HMPT react with TPCB with k = (6 ± 1) \times 10^9 1/mol s. Simultaneously with the decay of the optical absorption of the solvated electrons, the formation of the absorption of t-stilbene (at 300 nm) and that of stilbene radical anions (at 500 nm) was observed. Thus, it is concluded that TPCB is undergoing a dissociative electron attachment process e\textsubscript{solv} + TPCB \rightarrow t-St + t-St\textsuperscript{-}.

The lifetime of a possible intermediate (TPCB\textsuperscript{-}) was estimated as being smaller than 10\textsuperscript{-9} s. The 100 eV yield of t-stilbene was determined as G(t-St) = 3.4.

Experimental

r-1, c-2, t-3, t-4-tetraphenylcyclobutane (TPCB) was prepared by UV irradiation of t-stilbene in benzene solution [6] and recrystallized three times from ethanol solution and dried under high vacuum (m.p. 163.8—164.3 °C). Hexamethylphosphoric triamide (Merck-Schuchardt, p.a. 99\%\textsubscript{o}) was purified as described earlier [2]. Dilute solutions of TPCB in HMPT were irradiated in rectangular quartz cells (light path: 2 cm) with 20 ns pulses of 16 MeV electrons from an L-band linear accelerator (Vickers Co. Ltd.). The optical detection method was used. The analyzing light produced by a xenon lamp (XBO 450 W, Osram) passed appropriate cut-off filters before reaching the sample cell. The samples were freed from oxygen either by several freeze-pump-thaw cycles or by bubbling for 30 minutes with purified argon. In all cases samples were irradiated with only one or two pulses in order to make sure that t-stilbene formed during the irradiation did not interfere. For the determination of the absorbed dose per pulse the Fricke dosimeter was used (O\textsubscript{2}-saturated solutions, G(Fe\textsuperscript{3+}) = 13.0 [7]).

Figure 1 shows optical absorption spectra obtained about 1 µs, 200 µs, and 1 ms after irradiation of an oxygen-free TPCB solution (1.1 x 10\textsuperscript{-3} mol/l) in HMPT. Immediately after the 20 ns pulse the absorption of solvated electrons (e\textsubscript{solv}) was observed. Simultaneously with the decay of the absorption of the solvated electrons, the spectrum A in Fig. 1

Introduction

Hexamethylphosphoric triamide (HMPT) has been proved to be an appropriate solvent for the investigation of reactions of negatively charged ion molecules generated during the irradiation of liquid systems with high energy radiation. We reported recently [1, 2] on the generation and reaction of radical anions of β-nitrostyrene upon irradiation of HMPT solutions containing small amounts of β-nitrostyrene with 50 ns pulses of 16 MeV electrons produced by a linear accelerator.

This paper describes results obtained upon irradiating dilute HMPT solutions of r-1, c-2, t-3, t-4-tetraphenylcyclobutane (TPCB). The latter compound is known to be fragmented rather effectively into stilbene during the irradiation with UV-light [3, 4]:

\[ C_6H_5 \rightarrow \text{H}_2 \rightarrow C_6H_5 \]

Recent flash photolysis experiments showed that this 2σ → 2π cleavage occurs with a rate constant k > 10\textsuperscript{8} s\textsuperscript{-1} [5]. In the following it is reported that TPCB is also fragmented forming essentially t-stilbene under the influence of high energy radiation in HMPT solution via an anionic mechanism.

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It may be emphasized that this rate constant is definitely smaller than that of the reaction

\[ e^-_{\text{solv}} + \text{t-stilbene} \rightarrow ((3 \pm 1) \cdot 10^{10}) \text{mol/s} \]

in HMPT [8].

Upon investigating the fate of the absorption formed by the reaction of solvated electrons with TPCB the bands between 280 and 350 nm with peaks at 300 and 310 nm were found to be permanent. The absorption at \( \lambda > 350 \text{ nm} \) decayed completely with a first half-life of ca. 0.6 ms. Neither second nor first-order kinetic treatments yielded an unequivocal correlation of the decay of the absorption to a single process indicating a rather complex reaction mechanism. As can be seen from the oscilloscope traces in Fig. 4, an additional absorption is formed at \( \lambda < 350 \text{ nm} \), simultaneously with the decay of the absorption at \( \lambda > 350 \text{ nm} \). It was, furthermore, found that the total permanent optical density between 280 and 350 nm increased was formed indicating the occurrence of the reaction

\[ e^-_{\text{solv}} + \text{TPCB} \rightarrow (\text{TPCB})^- \]  \hspace{1cm} (2)

Typical oscilloscope traces demonstrating the decay of \( e^-_{\text{solv}} \) and the formation of a new product are presented in Figure 2. As will be explained below the spectrum A in Fig. 1 could not be correlated to the intermediate \((\text{TPCB})^-\).

It was found that the decay of the \( e^-_{\text{solv}} \)-absorption and the formation of the new absorption were following pseudo-first-order kinetics, the reciprocal lifetimes \( \tau^{-1} \) depending linearly on the concentration of TPCB. The rate constant

\[ k( e^-_{\text{solv}} + \text{TPCB}) = (6 \pm 1) \cdot 10^{10} \text{mol/s} \]

was evaluated from plots of \( \tau^{-1} \) vs. [TPCB] (see Figure 3).

![Fig. 1. Optical absorption spectra obtained 1 \( \mu \text{s} \) (A), 200 \( \mu \text{s} \) (B) and 1 ms (C) after the irradiation of a HMPT solution of TPCB (1.1 \( \times 10^{-3} \) mol/l) with a 20 ns pulse of 16 MeV electrons. Absorbed dose per pulse: 2.6 \( \times 10^3 \) rad.](image)

![Fig. 2. Typical oscilloscope traces demonstrating the decay of the absorption of solvated electrons at \( \lambda = 1070 \text{ nm} \) (a) and the formation of the absorption of the product of the reaction \( e^-_{\text{solv}} + \text{TPCB} \) at \( \lambda = 500 \text{ nm} \) (b). TPCB (3.5 \( \times 10^{-4} \) mol/l) in HMPT at room temperature. Absorbed dose per pulse: 2.0 \( \times 10^3 \) rad. Pulse duration: 20 ns.](image)

![Fig. 3. Plot of the reciprocal lifetime of the increase of the optical density at \( \lambda = 500 \text{ nm} \) (after a 20 ns pulse of 16 MeV electrons) as a function of the TPCB concentration. Absorbed dose per pulse: 2.6 \( \times 10^3 \) rad.](image)

![Fig. 4. Typical oscilloscope traces demonstrating the decrease of the absorption at 500 nm (a) and the increase of the absorption at 300 nm (b). [TPCB]: 1.1 \( \times 10^{-5} \) mol/l. Absorbed dose per pulse: 2.6 \( \times 10^3 \) rad. Pulse duration: 20 ns.](image)
Fig. 5. (a) Optical absorption spectra obtained 10 min after the irradiation of HMPT solutions of TPCB (1.0 \times 10^{-3} \text{ mol/l}) with various numbers of pulses (2.6 \times 10^3 \text{ rad per pulse}). The number of pulses is indicated at the spectra. (b) Plot of the optical density at 300 nm vs. the number of pulses.

The analysis of the optical absorption spectra yielded the following: with respect to the spectrum of t-stilbene the permanent absorption between 280 and 350 nm with the peaks at 300 and 310 nm is assigned to t-stilbene [9]. By comparing the transient absorption at $\lambda > 350$ nm with absorption spectra of radical anions of t-stilbene (t-St$^-$) and c-stilbene (c-St$^-$) reported in the literature [10, 11] it appears that the peak at 500 nm is correlated both to t-St$^-$ and c-St$^-$. The peaks at 670 nm and 750 nm correspond to t-St$^-$ and c-St$^-$. It should be emphasized that the absorption at $\lambda > 350$ nm and the major portion of the final t-stilbene absorption (about 70%) are formed simultaneously. The yield of t-stilbene calculated from the absorption at 300 nm ($\varepsilon = 2.8 \times 10^4$ \text{ l/mol cm}) [9] is of the same magnitude as that of t-stilbene radical anion ($\varepsilon = 5.2 \times 10^4$ \text{ l/aol cm}) [11]. Furthermore, it may be recalled that the decay of the absorption of the solvated electrons is accompanied by the simultaneous formation of the new absorption after the pulse.

Thus, it is concluded that upon the addition of an electron the rapid fragmentation of a TPCB molecule is caused ("dissociative electron attachment") according to the following mechanism:

$$e_{\text{solv}} + \text{TPCB} \rightarrow k(e_{\text{solv}} + \text{TPCB})/\text{(TPCB}^-), \quad (2)$$

$$\text{(TPCB}^-) \rightarrow t\text{-St}^- + t\text{-St}, \quad (3a)$$

$$\rightarrow c\text{-St}^- + c\text{-St}. \quad (3b)$$

The lifetime of (TPCB$^-$) is assumed to be shorter than $10^{-9}$ s since reaction (2) was found to be always the rate determining step for the formation of stilbene radical anions. From the fact that a rather strong absorption around 750 nm was observed (spectrum A in Fig. 1) the occurrence of reaction (3b) was conjectured. However, only a minor fraction of the total conversion of TPCB is assumed to be due to processes involving reaction (3b) since the radiation chemical yield of t-stilbene is rather high ($G(t\text{-St}) = 3.4$), as evaluated from the total absorption at 300 nm (Figure 5(b)). Since in HMPT $G(e_{\text{solv}})$ is 2.3 [12], the maximum attainable value of $G(t\text{-St})$ would be 4.6 (if each solvated electron causes the formation of two t-stilbene molecules). The fact that the measured $G(t\text{-St})$ value corresponds to about 74% of the maximum attainable value indicates that the major portion of solvated electrons initiates the decomposition of TPCB molecules into t-stilbene. The finding that $G(t\text{-St})$ is definitely smaller than the maximum attainable value might be explained by the occurrence of reaction (3b) and by the fact that only a certain fraction of stilbene radical anions are neutralized according to reaction (4):

$$t\text{-St}^- + S^+ \rightarrow t\text{-St} + S \quad (4)$$

($S^+$: radical cations of solvent molecules S).

An additional formation of t-stilbene was observed by the slow formation of the absorption at 300 nm in Figure 4(b). This corresponds to the decay of the absorption at 500 nm (Figure 4(a)). The rest of the stilbene radical anions is undergoing reactions (not yielding stilbene) which could not be identified during this investigation.

In conclusion it may be stated that TPCB reacts rather rapidly with solvated electrons in HMPT solution via a dissociative electron attachment.
process. t-stilbene is formed as the major reaction product.

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