JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 6, 545–550 (1993)

PHOTOCHLORINATION OF TETRACHLOROETHENE IN CARBON TETRACHLORIDE SOLUTIONS

J. S. MILLER AND S. LEDAKOWICZ

Faculty of Process and Environmental Engineering, Technical University of Łódź, ul. Wólczańska 175, 90-924 Łódź, Poland

Validation of the mechanism of tetrachloroethene photochlorination at low C_2Cl_4 concentrations was investigated. The reaction was examined in carbon tetrachloride solution. For initial tetrachloroethene concentrations below 2 mol l^{-1}, the solvent participates in a free-radical chain photochlorination. The presence of CCl_4 disturbs the course of this particular chain reaction and influences the duration of the induction period.

INTRODUCTION

The mechanism of tetrachloroethene photochlorination in the absence of solvent is well established.[1,2] If the only initiation step is the photolysis of chlorine molecules, this chain reaction involves the following elementary steps:

$$Cl_2 + h\nu \rightarrow 2Cl^{\bullet} \qquad \varphi I \qquad (1)$$

$$Cl^{\bullet} + C_2Cl_4 \rightarrow C_2Cl_5^{\bullet} \qquad k_2(BX) \qquad (2)$$

$$C_2Cl_5^{\bullet} + Cl_2 \rightarrow C_2Cl_6 + Cl^{\bullet} \qquad k_3(AY) \qquad (3)$$

$$2C_2Cl_5^{\bullet} \rightarrow 2C_2Cl_4 + Cl_2 \qquad k_4(Y^2) \qquad (4)$$

$$\quad \llcorner\!\rightarrow C_2Cl_6 + C_2Cl_4 \qquad (4a)$$

$$C_2Cl_5^{\bullet} + Cl^{\bullet} \rightarrow C_2Cl_4 + Cl_2 \qquad k_5(XY) \qquad (5)$$

$$\quad \llcorner\!\rightarrow C_2Cl_6 \qquad (5a)$$

$$2Cl^{\bullet} \rightarrow Cl_2 \qquad k_6(X^2) \qquad (6)$$

The last two termination steps [equations (5) and (6)] can be neglected owing to the excess of tetrachloroethene. Applying the Bodenstein rule and the long-chain approximation for the first four equations, one can obtain a kinetic equation in the form

$$-\frac{dA}{dt} = \frac{dC}{dt} = r = \frac{k_3}{k_4^{0\cdot5}} (\varphi I)^{0\cdot5} A \qquad (7)$$

This simple expression shows that the reaction is first order with respect to chlorine, zero order with respect to C_2Cl_4 and 0·5 order with respect to the light intensity.

In the absence of solvent, the reaction course is restricted to conversion levels below about 30% (with respect to C_2Cl_4) owing to precipitation of the reaction product. The presence of solid hexachloroethane in the reaction mixture distinctly disturbs this photochemically initiated reaction. The solubility of C_2Cl_6 in tetrachloroethene is 2·74 mol l^{-1} and in carbon tetrachloride 2·69 mol l^{-1} (293 K).[3] Therefore, in order to achieve high conversion levels, a low initial tetrachloroethene concentration in carbon tetrachloride should be used.

The photochlorination of tetrachloroethene in carbon tetrachloride solutions should proceed according to the same mechanism as in neat C_2Cl_4. Only as a result of changes in the ratio of the substrate concentrations may another possible termination reaction play some role [equations (5) and (6)].

The first work on tetrachloroethene photochlorination in carbon tetrachloride solutions was published by Leermakers and Dickinson[4] in 1932. Since then, some questions have been answered. We know that participation of $Cl_3^{\bullet}$ radicals is virtually impossible[5] and the telomerization reaction of C_2Cl_4 is unrealistic owing to steric obstacles.[6] However, some problems are still not clear, such as the discrepancy in the mass balance of chlorine. The aim of this work was to examine the reaction course at low initial tetrachloroethene concentrations and to try to explain the behaviour of the system.

EXPERIMENTAL

The experiments were carried out in a 4·3 cm i.d. and 0·15 l capacity stirred cell equipped with a cooling jacket. The reactor, made of Pyrex glass, was surrounded with four light sources (LF 6W glow tubes, manufactured by Polam, Poland) with an emission range of 360–620 nm of the continuous-type spectrum.

0894-3230/93/100545-06$08.00

Received 5 January 1993
Revised 7 May 1993

The necessary precautions were taken to avoid daylight initiation of the photoreaction. The light intensity within the reaction liquid was determined by uranyl oxalate actinometry.[7] The details of actinometric measurements for polychromatic light have been given elsewhere.[8] The various light intensities were obtained by changing the distance between the lamp and reactor. The value of the chlorine quantum yield was assumed to be 0·5.[3,9] The desirable substrate concentrations were prepared by mixing in appropriate ratios carbon tetrachloride saturated with chlorine with solutions of tetrachloroethene in carbon tetrachloride.

The experiments were performed in the stationary mode. The reaction temperature was controlled (± 1 K) by circulating water at constant temperature in the range 293–329 K.

Chlorine concentrations in the sample were determined by the iodimetric method using acidic potassium iodide in excess and back-titrating the liberated iodine with sodium thiosulphate. The error in the titration did not exceed 0·01 mol l^{-1}.

The hexachloroethane and tetrachloroethene contents in the reaction sample were determined by gas chromatographic (GC) analysis. During each experiment samples of the liquid reaction mixture were removed through the sample port into a flask containing acetone. The sampling time was negligible compared with the reaction time. The unreacted chlorine or chloroacetones were desorbed using a reflux condenser and bubbling argon through the sample for 1 min. No traces of C_2Cl_6 were observed on the condenser walls. The parameters of GC analysis were as follows: stainless-steel column, 3 m × 4 mm i.d.; column filling, 3% OV-17 deposited Chromosorb G (60–80 mesh); injector temperature, 463 K; column temperature, 443 K; flame ionization detector temperature, 473 K; argon flow-rate, 5×10^{-4} l s^{-1}; and internal standard 0·1 M tetralin in acetone solution. The estimated accuracy of the GC analyses was 95–96%.

The mechanical stirring rate was set at 130 rpm. The light intensity absorbed in the reaction mixture ranged from $15\cdot42 \times 10^{16}$ to $138\cdot9 \times 10^{16}$ quanta $s^{-1} l^{-1}$. The initial chlorine concentration was 1·23, 0·85 and 0·57 mol l^{-1} and the range of initial tetrachloroethene concentration was between 3·26 and 0·98 mol l^{-1}.

RESULTS AND DISCUSSION

Assuming that all consumed chlorine yielded hexachloroethane:

$$A = A^0 - C \tag{8}$$

and integrating equation (7), we obtain a typical first-order kinetic relationship

$$\ln(A^0 - C) = \ln A^0 - kt \tag{9}$$

where

$$k = k_3/k_4^{0\cdot5}(\varphi I)^{0\cdot5}$$

which allows the value of reaction rate constant, k, to be calculated simply. The term ln A^0 does not relate to the true value of the initial chlorine concentration because it includes the error derived from an induction period.

For initial C_2Cl_4 concentrations 2·46 and 3·26 mol l^{-1}, the straight-line relationships $k \sim I^{0\cdot5}$ (Figure 1) and $r^0 \sim A^0$ (Figure 2) confirm the validity of

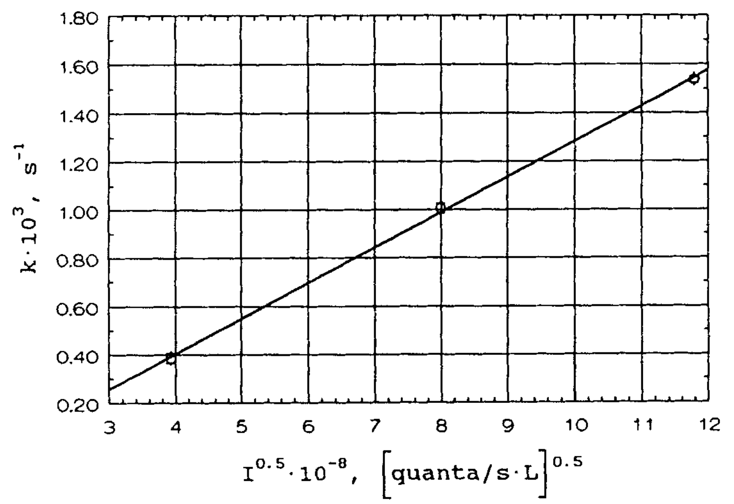

Figure 1. Dependence of the reaction rate constant on the square root of light intensity. $T = 293$ K; $A^0 = 1\cdot23$ mol l^{-1}; $B^0 = 3\cdot26$ mol l^{-1}

the assumed reaction mechanism and of the kinetic orders of reaction.

The dependence of the reaction rate constants on temperature in the range 293–323 K leads to an Arrhenius plot with the following pre-exponential factor and activation energy ($B^0 = 3{\cdot}26\ \mathrm{mol\,l^{-1}}$, $A^0 = 0{\cdot}57\ \mathrm{mol\,l^{-1}}$, $I = 63{\cdot}93 \times 10^{16}\ \mathrm{quanta\,s^{-1}\,l^{-1}}$:

$$k = k_0 \exp\left(\frac{-E}{RT}\right)(\varphi I)^{0\cdot5} \qquad (10)$$

$$k_0 = (1{\cdot}259 + 0{\cdot}762) \times 10^9\ \mathrm{l^{0\cdot5}\,s^{-0\cdot5}\,mol^{-0\cdot5}}$$

$$E = 50{\cdot}23 \pm 2{\cdot}76\ \mathrm{kJ\,mol^{-1}}$$

which is close to that obtained for the reaction without solvent and activation energy $55{\cdot}55\ \mathrm{kJ\,mol^{-1}}$.[3]

The calculated quantum yield of the overall reaction of tetrachloroethene chlorination in CCl_4 solutions changes from 820 to 3250, indicating that the long-chain approximation is correct.

However, for $B^0 < 2\ \mathrm{mol\,l^{-1}}$ we observed an unusual behaviour of the system. The means of increasing the amount of C_2Cl_6 during the reaction is not typical of a free-radical chain reaction as illustrated in Figure 3. Figure 4 shows the changes in the concentrations of all the reagents with time. A and B change symmetrically

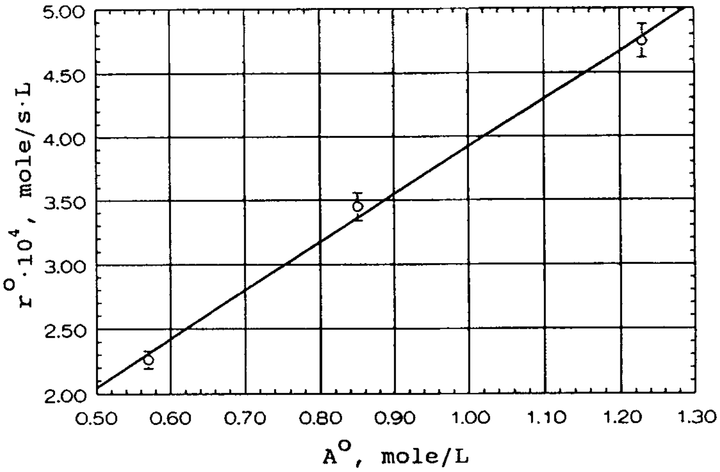

Figure 2. Dependence of reaction rate on initial chlorine concentration. $T = 293$ K; $I = 15{\cdot}42 \times 10^{16}\ \mathrm{quanta\,s^{-1}\,l^{-1}}$; $B^0 = 3{\cdot}26\ \mathrm{mol\,l^{-1}}$

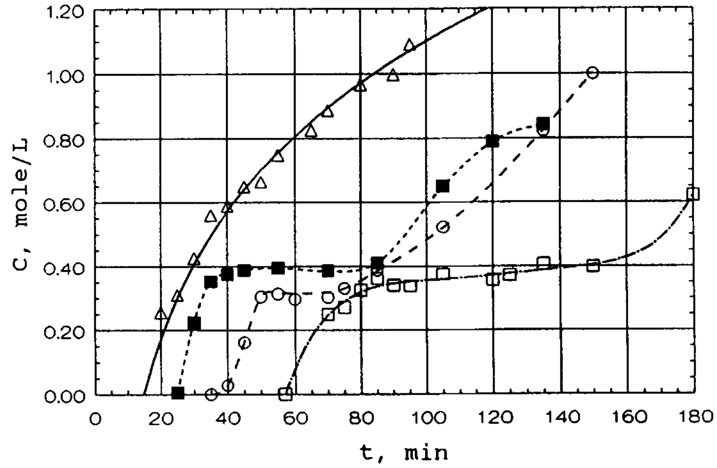

Figure 3. Changes in hexachloroethane concentration during reaction for $B^0 =$ (△) 3·26, (○) 1·96 and (□) 0·98 $\mathrm{mol\,l^{-1}}$ with $I = 15{\cdot}42 \times 10^{16}\ \mathrm{quanta\,s^{-1}\,l^{-1}}$ and (■) 0·98 $\mathrm{mol\,l^{-1}}$ with $I = 63{\cdot}93 \times 10^{16}\ \mathrm{quanta\,s^{-1}\,l^{-1}}$. $T = 293$ K

to C and during the induction period the chlorine concentration increases and then decreases.

Figure 5 shows the dependence ln $A \sim t$ [equation (9)] for various initial concentrations of C_2Cl_4. Equation (9) is fulfilled by only a few points determined in the initial period of the reaction for $B^0 = 1{\cdot}96$ and $0{\cdot}98 \text{ mol l}^{-1}$, and straight lines are not parallel to those for $B^0 = 3{\cdot}26$ and $2{\cdot}46 \text{ mol l}^{-1}$. This shows that the reaction order with respect to tetrachloroethene is not zero. Moreover, equation (8) is invalid. The chlorine content in the reaction mixture is several percent higher than that resulting from the difference of the initial amount of chlorine, A^0, and the amount of hexachloroethane obtained. This discrepancy was also reported by Leermakers and Dickinson,[4] but their explanation can no longer be accepted. This strange reaction course for $B^0 < 2 \text{ mol l}^{-1}$ leads to the conclusion that photochlorination in the presence of CCl_4 follows another mechanism. Leermakers and Dickinson[4] suggested that the reaction rate did not depend on the square root of the light intensity. Probably the dominant role of the square termination reaction by recombination of pentachloroethene radicals [equation (4)] is violated. Under these conditions for gas-phase

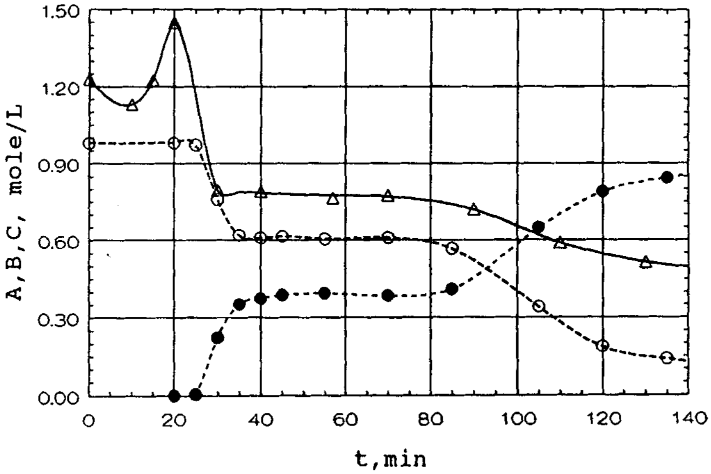

Figure 4. Dependence of reactant concentrations on reaction time: (△) Cl_2; (○) C_2Cl_4; (●) C_2Cl_6. $T = 293$ K; $I = 63{\cdot}93 \times 10^{16} \text{ quanta s}^{-1}\text{l}^{-1}$

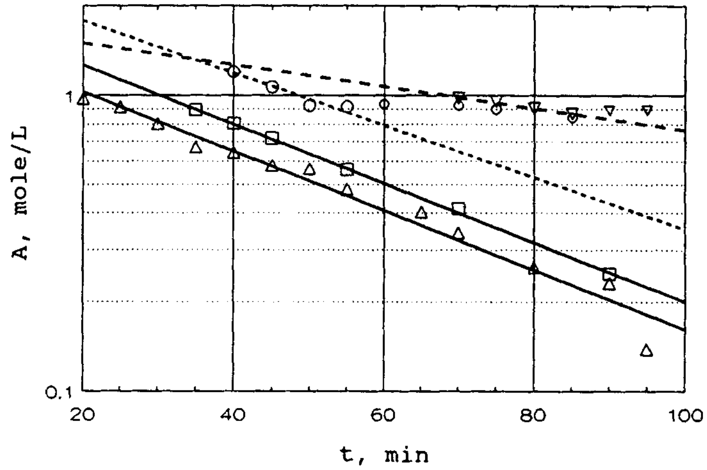

Figure 5. Equation (9) for initial tetrachloroethene concentrations B^0 = (△) 3·26, (□) 2·46, (○) 1·96 and (▽) 0·98 mol l^{-1}. $T = 293$ K; $I = 15{\cdot}42 \times 10^{16} \text{ quanta s}^{-1}\text{l}^{-1}$

reactions linear termination with the vessel walls or a third body is often taken into consideration. This 'third body' here can be a carbon tetrachloride solvent molecule. In order to prove this hypothesis, electron paramagnetic resonance (EPR) investigations of the systems CCl_4 and CCl_4–Cl_2 were carried out. The radicals were induced photochemically and, owing to their low stability at room temperature, the measurements were performed at the temperature of liquid nitrogen (77 K).

The photolysis of carbon tetrachloride demands light energy corresponding to a wavelength of 280 nm:[7,10]

$$CCl_4 \xrightarrow{h\nu'} CCl_3^{\bullet} + Cl^{\bullet} \qquad (11)$$

Figures 6(a) and (b) present the EPR spectra of carbon tetrachloride unirradiated and irradiated with light of wavelength below 280 nm. The peak in Figure 6(b) shows $CCl_3^{\bullet}$ radicals, confirmed by its position relative to standard DPPH (1,1-diphenyl-2-picrylhydrazyl). Irradiation of a CCl_4 sample through the Pyrex glass walls which cuts off ultraviolet light below 280 nm, does not lead to a $CCl_3^{\bullet}$ band and the result is the same as in Figure 6(a). The EPR spectra in Figure 6(c) and (d) were obtained with solutions of chlorine in CCl_4. The EPR spectrum of the system Cl_2–CCl_4 [Figure 6(c)] is the same as that of CCl_4 without Cl_2 [Figure 6(a)]. After irradiation of the solution of chlorine in carbon tetrachloride through the Pyrex glass, the band for $CCl_3^{\bullet}$ radicals appeared [Figure 6(d)]. As the light used can only homolyse chlorine molecules, the trichloromethyl radicals probably arise from the sensitizing action of chlorine atoms according to

$$Cl_2 + h\nu \rightarrow 2Cl^{\bullet} \qquad (1)$$

$$CCl_4 + Cl^{\bullet} \rightarrow CCl_3^{\bullet} + Cl_2 \qquad (12)$$

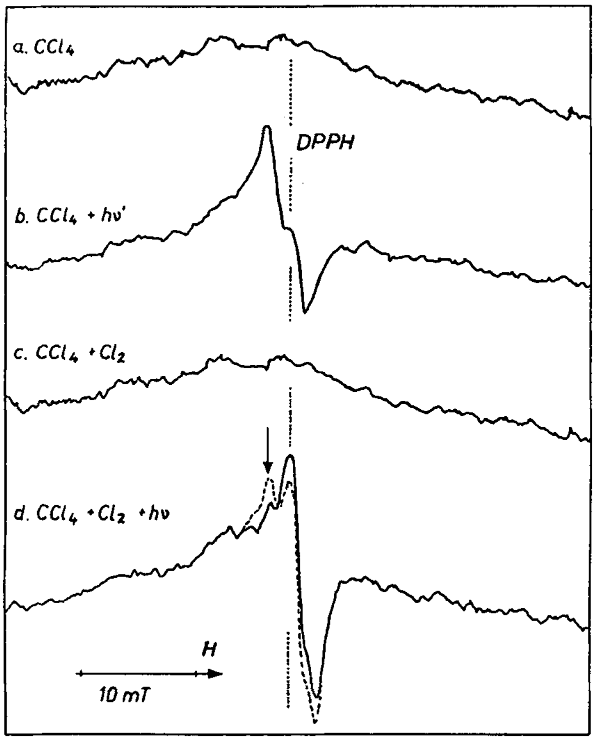

Figure 6. EPR spectra (see text). Microwave power = 10 mW; $T = 77$ K

The band for chlorine atoms is apparent on the low-field side of the spectrum. The EPR signals of both samples, CCl_4 and CCl_4–Cl_2 represent the superposition of the $Cl^{\bullet}$ and $CCl_3^{\bullet}$ radical spectra. In the first case [Figure 6(b)] the singlet of the $CCl_3^{\bullet}$ radical is more evident than in the second case [Figure 6(d)] where the presence of chlorine influenced the intermolecular action, hence the peak of $CCl_3^{\bullet}$ is not so distinct. In order to confirm that the small peak depicted by an arrow in Figure 6(d) originates from $CCl_3^{\bullet}$ radicals, the same sample of CCl_4–Cl_2 was additionally irradiated without a glass diaphragm. As shown by a broken line in Figure 6(d), the amount of $CCl_3^{\bullet}$ radicals increased and the spectrum became clearer.

On the basis of preliminary EPR measurements, the participation of CCl_4 in photochlorination of tetrachloroethene is very probable. The reaction scheme in equations (1)–(6) can be completed with the following elementary reactions, which have been reported in the literature:[11–16]

$$Cl^{\bullet} + CCl_4 \rightarrow Cl_2 + CCl_3^{\bullet} \qquad (12)^{11}$$

$$C_2Cl_5^{\bullet} + CCl_4 \rightarrow C_2Cl_6 + CCl_3^{\bullet} \qquad (13)^{12}$$

$$CCl_3^{\bullet} + CCl_4 \rightarrow C_2Cl_6 + Cl^{\bullet} \qquad (14)^{13}$$

$$\hookrightarrow Cl_2 + C_2Cl_5^{\bullet} \qquad (14a)$$

$$CCl_3^{\bullet} + Cl_2 \rightarrow CCl_4 + Cl^{\bullet} \qquad (15)^{14}$$

$$CCl_3^{\bullet} + C_2Cl_6 \rightarrow CCl_4 + C_2Cl_5^{\bullet} \qquad (16)$$

$$CCl_3^{\bullet} + C_2Cl_5^{\bullet} \rightarrow C_2Cl_4 + CCl_4 \qquad (17)$$

$$CCl_3^{\bullet} + Cl^{\bullet} \rightarrow CCl_4 \qquad (18)^{14}$$

$$2CCl_3^{\bullet} \rightarrow C_2Cl_6 \qquad (19)^{15,16}$$

$$\hookrightarrow C_2Cl_4 + Cl_2 \qquad (19a)$$

Participation of carbon tetrachloride in the photochlorination of tetrachloroethene is apparent at low C_2Cl_4 concentrations, where some of the above reaction steps [equations (12)–(19)] are predominant. The solution of the kinetic equations is very difficult, mainly owing to the non-applicability of a quasi steady-state approximation. Therefore, a qualitative explanation of the strange reaction course is attempted here.

The observed dependence of the induction period on the initial concentration of $\mathrm{C_2Cl_4}$, and hence also on carbon tetrachloride concentration, follows from the run of competitive reactions of chlorine atom with $\mathrm{CCl_4}$ [equation (12)] and with tetrachloroethene [equation (2)]. In the initial reaction period the increase in chlorine concentration observed in Figure 4 may be due to the dominance of reaction step (12) over reaction step (2). After the equilibrium has been attained following reaction (12) and the reverse of reaction (15), the pentachloroethene radicals formed start a chain reaction according to steps (2) and (3) (an initial sharp increase in product concentration in Figure 4). As the substrate ($\mathrm{Cl_2, C_2Cl_4}$) concentrations decrease the equilibrium for the reversible reaction [equations (12) and (15)] $\mathrm{Cl^{\bullet} + CCl_4 \rightleftharpoons Cl_2 + CCl_3^{\bullet}}$ is shifted to the right. The accumulated $\mathrm{CCl_3^{\bullet}}$ radicals start to participate in the main reaction chain [reaction steps (17) and (18)] and production of hexachloroethane slows. Under these circumstances, dynamic equilibrium is attained: the chlorine atoms and pentachloroethene radicals formed are used up in reaction steps (17) and (18) [or also (19a)], producing substrates and consuming $\mathrm{CCl_3^{\bullet}}$ radicals. Hence the concentrations of the reagents remain unchanged (the plateau observed in Figure 4). As the concentrations of $\mathrm{CCl_3^{\bullet}}$ radicals decrease, the propagation steps (2) and (3) start to dominate again and the product concentration increases again.

The reaction chain may consist of other reactions forming $\mathrm{C_2Cl_6}$ with the participation of $\mathrm{CCl_4}$ as well, e.g. equations (1), (2) and (12)–(15).

It is also worth considering in this unusual reaction the physical interaction of the solvent with radicals (chain carriers), i.e. a so-called 'cage effect,' known also as a diffusion cage effect.[17] The chlorine radicals generated in initiation and propagation steps, in addition to recombination, may react with solvent molecules. The diffusion rate of radicals is very low and their reactivity is very high, and if they have no partner in the cage they react in their vicinity. This can be manifested by increasing the duration of the induction period and of the stationary reagent concentrations (Figure 4).

SYMBOLS

A, B, C	molar concentrations of chlorine, tetrachloroethene and hexachloroethane, respectively
E	activation energy
h	Planck's constant
I	light intensity
k_0	pre-exponential factor
k, k_i	reaction rate constant
R	universal gas constant
r	reaction rate
T	temperature
t	time
X, Y	molar concentration of chlorine and pentachloroethene radicals, respectively
φ	quantum yield
ν	frequency of UV radiation
0	superscript referring to initial value

REFERENCES

1. M. L. Poutsma, in *Methods in Free-Radical Chemistry*, edited by E. R. Huyser, Vol. 1. Marcel Dekker, New York (1969).
2. N. M. Emanuel and D. G. Knorre, *Kinetyka chemiczna w układach jednorodnych*. PWN, Warsaw (1983).
3. J. S. Miller, PhD Thesis, Łódź Technical University (1991).
4. J. A. Leermakers and R. G. Dickinson, *J. Am. Chem. Soc.* **54**, 4648–4657 (1932).
5. J. A. Kiryushin and V. A. Poluektov, *Kinet. Katal.* **16**, 288–295 (1975); F. W. Breitbarth and S. Rottmayer, *Plasma Chem. Plasma Process.* **6**, 381–387 (1986).
6. M. L. Poutsma and R. L. Hinman, *J. Am. Chem. Soc.* **86**, 3807–3814 (1964).
7. J. G. Calvert and J. N. Pitts, Jr, *Photochemistry*. Wiley, New York (1966).
8. J. Perkowski and J. S. Miller, *Tenside Detergents* **21**, 7–9 (1984).
9. O. M. Alfano and E. A. Cassano, *Ind. Eng. Chem. Res.* **27**, 1095–1103 (1988).
10. M. S. Kharasch, E. V. Jensen and W. H. Urry, *J. Am. Chem. Soc.* **69**, 1100–1105 (1947).
11. P. Goldfinger, M. Jehunehomme and G. Martens, *J. Chem. Phys.* **29**, 456–458 (1958).
12. D. C. Nonhebel and J. C. Walton, *Free Radical Chemistry*, p. 83. Cambridge University Press, Cambridge (1974).
13. A. Horowitz and L. A. Rajbenbach, *J. Phys. Chem.* **74**, 678–681 (1970).
14. G. R. De Mare and G. Huybrechts, *Trans. Faraday Soc.* **64**, 1311–1318 (1968).
15. K. U. Ingold, in *Free Radicals*, pp. 53–54, edited by J. Kochi, Vol. 1. Wiley, New York (1973).
16. H. J. Tiller, R. Mohr, D. Berg, F. W. Breitbarth, K. Dumke and R. Goebel, *Beitr. Plasmaphys.* **21**, 329–335 (1981).
17. M. P. Ramage and R. E. Eckert, *Ind. Eng. Chem., Fundam.* **14**, 214–221 (1975).