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PULSE PHOTOLYSIS OF PbCl$_4$ IN NON-AQUEOUS SOLUTIONS


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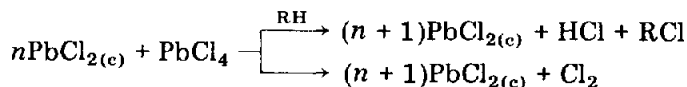
Summary

Lead(IV) chloride solutions in CCl$_4$, CHCl$_3$, cyclohexane, benzene, toluene, chlorobenzene, N,N-dimethylformamide and pyridine have been irradiated with an approximately 1.5 kJ pulse of UV radiation lasting 0.5 ms. The course of the photochemical processes has been followed by measuring the loss of PbCl$_4$, the changes of Cl$_2$ concentration and by identification of chlorination products. In a similar way, chlorine solutions in cyclohexane and benzene have been investigated. Primary processes are discussed in detail. The most probable process in solvents that do not form complexes with PbCl$_4$ is predissociation of the Pb−Cl bond

$$PbCl_4 + h\nu \rightarrow \cdot PbCl_3 + Cl$$
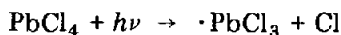
whereas in those forming complexes with PbCl$_4$ electron transfer takes place:

$$PbCl_4 \cdots ArH + h\nu_{CT} \rightarrow (\cdot PbCl_4^- \cdots ArH^{\cdot +})^*$$
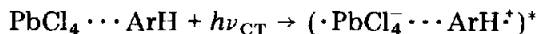
The results are compared with those obtained earlier under steady irradiation. This allows us to determine new pathways of secondary processes that are unobservable with the continuous illumination technique. The pathways include processes photoinduced by the phase of fresh finely dispersed PbCl$_2$ crystals:

$$nPbCl_{2(c)} + PbCl_4 \begin{array}{l} \xrightarrow{\text{RH}} (n+1)PbCl_{2(c)} + HCl + RCl \\ \xrightarrow{} (n+1)PbCl_{2(c)} + Cl_2 \end{array}$$

1. Introduction

Among the tetrahalides of Group IV elements, PbCl$_4$ is distinguished by its physical and chemical properties, in particular by its being an electron acceptor [1, 2]. For this reason it seemed worthwhile studying the photochemical behaviour of this compound, especially in systems in which electron donor−acceptor (EDA) interactions were likely to occur.

Reports on the photochemistry of $PbCl_4$ solutions in organic solvents [3 - 12] have dealt with processes initiated by steady sources of radiation. This work provides a continuation of our studies [12] and includes a summary of results obtained by employing a source of pulse radiation for investigation of the previously mentioned systems. The following advantages are offered by the pulse technique.

(1) Both in the liquid form and in solutions $PbCl_4$ is a thermodynamically unstable compound [13, 14] that is capable of undergoing thermal degradation even at room temperature. Consequently, results obtained using continuous irradiation were vitiated by the difficulty of estimating errors due to concurrent thermal reactions. Reduction of the irradiation time by a factor of 10^6 allowed us to eliminate the thermal effect.

(2) In many experiments the $PbCl_4$ solutions became turbid during prolonged steady illumination owing to precipitation of $PbCl_2$ crystals. This caused scattering of the radiation which made it impossible to obtain accurate measurements of such quantities as quantum yields. Under pulse irradiation the resulting crystals are not large enough to scatter the radiation effectively.

(3) Irradiation of secondary reaction products should be greatly reduced in the pulse technique.

(4) The use of a pulsed source of radiation has been found to initiate new, sometimes unexpected, pathways of secondary processes [15 - 18].

2. Experimental

Using previously described procedures benzene [13], CCl_4 [13], chlorobenzene [6], toluene [6], pyridine [8], N,N-dimethylformamide (DMF) [10] and chloroform [12] were purified. Analytical reagent grade cyclohexane was refluxed for 8 h with 20% oleum and for 8 h with a nitrating mixture (three parts concentrated HNO_3 to two parts concentrated H_2SO_4). After phase separation the cyclohexane layer was shaken with a 5% NaOH solution to remove the yellow colour, washed with water, dried with $MgSO_4$, refluxed for 10 h over sodium, distilled, the distillate shaken with a small amount of 50% H_2SO_4, washed with water, dried with $MgSO_4$ and doubly distilled from sodium over a 1 m Vigreux column. The main fraction had a transmittance of 100% for wavelengths above 270 nm (at a thickness of the solvent layer of 5 cm, against water) and was free of unsaturated and aromatic contaminants, as shown by UV spectrophotometry and by gas–liquid chromatography (GLC). The remaining reagents were of analytical grade and were used as supplied.

Solutions were irradiated at room temperature with a flash lamp in a laboratory-made irradiation assembly [19]. The quartz lamp (25 mm × 225 mm) was filled with argon at a pressure of 100 Torr. The pulse energy was up to 1.5 kJ and the pulse duration at half-height was of the order of

0.5 ms. A cylindrical quartz vessel (1 cm i.d. × 25 cm) was also used in which 1 cm liquid filters of radiation could be inserted. As liquid filters, either solvents or aqueous cobalt(II) or nickel(II) solutions were used, *e.g.* a solution comprising 300 g $CoCl_2 \cdot 6H_2O$ and 240 g $NiCl_2 \cdot 6H_2O$ per cubic decimetre was used for $\lambda = 300$ nm and a solution of 500 g $Co(NO_3)_2 \cdot 6H_2O$ per cubic decimetre for $\lambda = 360$ nm [19]. The quantity of absorbed photons was measured by means of a Parker actinometer [20].

Lead(IV) chloride was obtained as described elsewhere [9]. Selection of appropriate concentrations of $PbCl_4$ was important for ensuring almost identical absorption of the actinometric and $PbCl_4$ solutions. The concentrations of $PbCl_4$ solutions for appropriate wavelengths of absorbed radiation were determined from molar absorption coefficients of the actinometric and $PbCl_4$ solutions and by assuming a constant concentration of the actinometric solution (0.006 M). The $PbCl_4$ concentrations varied from 5×10^{-3} to 5×10^{-4} M with the solvent used.

An aliquot of the solution was irradiated with one, or occasionally five, pulses and both solutions (the irradiated and the non-irradiated one) were centrifuged for 300 s at 60 rev s^{-1} to remove $PbCl_2$ crystals. This procedure was used in all cases, except for the pyridine and DMF solutions in which $PbCl_2$ was fairly soluble. From both solutions aliquots were withdrawn for assaying $PbCl_4$, oxidants ($PbCl_4 + Cl_2$) and chloride ions. The oxidants were assayed iodometrically. After evaporation of the solvent which caused decomposition of $PbCl_4$ to $PbCl_2$ and Cl_2, the residue ($PbCl_2$) was assayed complexometrically. Cl^- ions were assayed mercurometrically. From differences in concentrations of the non-irradiated and irradiated solutions losses of compounds were calculated and quantum yields φ_{Pb} and φ_{ox} for the loss of $PbCl_4$ and of the oxidants, respectively, were obtained using the actinometer. The remaining volumes were shaken with 1 M Na_2SO_3 or $(NH_4)_2Fe(SO_4)_2$ solutions, washed with water and dried with $MgSO_4$. After removing the $MgSO_4$ they were analysed using GLC.

Similarly, chlorine solutions in cyclohexane and benzene were prepared and irradiated. The solvents were saturated with chlorine, which was dried by passing through concentrated H_2SO_4 and through a P_2O_5 tube, up to a concentration of approximately 10^{-2} M. The solutions were then irradiated with one pulse, the loss of chlorine was determined iodometrically, chlorine was removed and the products of photochlorination of the solvents were determined.

GLC analyses were run on a Pye Unicam Model 104 gas chromatograph equipped with a flame ionization detector. Columns were packed with 3% OV-1 on Diatomite CQ, 3% OV-101 on Celite, 10% Squalane on Celite and 10% Igepal on Celite for analysing products in the benzene and cyclohexane solutions and with 10% PEG 20M on Diatomite C-AW and 10% Ukon LB 550 on Celite alkalysed with 2% KOH for analysing products in the chlorobenzene and toluene solutions. Quantitative assays using GLC were accomplished by measuring peak areas using internal standards.

TABLE 1

Results of the pulse photolysis of the PbCl$_4$ solutions in organic solvents

Solvent	λ_{max} (nm)	Average Pb(IV) loss [12]		Average loss of total oxidants [12] Pb(IV) + Cl$_2$		Organic products	Yield (mole n_{ox}^{-1})	Relative isomers ratio
		$n_{Pb} \times 10^6$ (mole)	φ_{Pb} (mole einstein^{-1})	$n_{ox} \times 10^6$ (mole)	φ_{ox} (mole einstein^{-1})			
CCl$_4$	360	1.2	0.17					
	300	2.4	0.38					
CHCl$_3$	360	1.9	0.24	1.2	0.15			
	300	3.3	0.59	1.6	0.29			
Cyclohexane	360	6.6	1.1	5.9	0.94	chlorocyclohexane	0.55	
	300	8.4	1.4	7.2	1.2	1,2-trans-dichlorocyclohexane	0.26	
	>210	20		17		dicyclohexyl	0.01	
Benzene	360	1.5	0.24	1.4	0.23			
	300	2.2	0.35	2.1	0.33			
	>280	2.6		2.3		chlorobenzene	0.82	
Chlorobenzene	360	0.66	0.11	0.64	0.10			
	300	1.1	0.18	0.97	0.16			
	>290	1.3		1.2		o-dichlorobenzene		$C_o:C_p = 1.1$
						p-dichlorobenzene		
Toluene[a]	>285			11.5		o-chlorotoluene	0.19	$C_o:C_{(m+p)};$
						m-+p-chlorotoluene	0.15	$C_\alpha = 1:0.78:3.3$
						benzyl chloride	0.65	
CCl$_4$ + toluene (c = 1 M)	420	1.5	0.50	0.48	0.16	o-chlorotoluene	0.17	$C_o:C_{(m+p)};$
	360	5.0	0.72	4.1	0.59	m-+p-chlorotoluene	0.10	$C_\alpha = 1:0.58:3.9$
	>285			7.5		benzyl chloride	0.67	

TABLE 1 (continued)

Solvent	λ_{max} (nm)	Average Pb(IV) loss [12]		Average loss of total oxidants [12] Pb(IV) + Cl$_2$		Organic products	Yield (mole n_{ox}^{-1})	Relative isomers ratio
		$n_{Pb} \times 10^6$ (mole)	φ_{Pb} (mole einstein^{-1})	$n_{ox} \times 10^6$ (mole)	φ_{ox} (mole einstein^{-1})			
CCl$_4$ + toluene (c = 0.1 M)	420	0.94	0.31	0.32	0.11			
	360	3.1	0.45	2.4	0.35			$C_o:C_{(m+p)}:$ $C_\alpha = 1:0.57:$
	>285					o-chlorotoluene		6.6
						m-+p-chlorotoluene		
						benzyl chloride		
DMF[b]	360			1.5	0.22			
	300			1.6	0.28			
Pyridine[b]	360			0.21	0.03			

[a] High rates of thermal reactions in toluene made the determination of quantum yields impossible. To determine these yields, toluene solutions in CCl$_4$ were employed.
[b] The Cl$^-$ concentration remains constant during irradiation.

3. Results

The $PbCl_4$ solutions in CCl_4, $CHCl_3$, cyclohexane, benzene, chlorobenzene, toluene, DMF and pyridine were irradiated in order to study systems in which either no intermolecular interactions occur or in which strong interactions between the components take place.

Quantum yields φ_{Pb} and φ_{ox} for the loss of $PbCl_4$ and of the sum of oxidants ($PbCl_4 + Cl_2$), respectively, [12] as well as identified organic products of photochlorination of the solvents are listed in Table 1. The data in the table, as well as observations made during this study, allow the following conclusions to be drawn. Almost all of the systems studied, except the DMF and pyridine systems, became turbid owing to formation of $PbCl_2$ crystals. The intensity of the turbidity increased with time as could be observed visually. In all cases the φ_{Pb} values are greater than the φ_{ox} values. If we assume that the loss of the oxidants is due to chlorination of the solvent, the difference $\varphi_{Pb} - \varphi_{ox}$ will determine the quantum yield for decomposition of $PbCl_4$ to $PbCl_2$ and chlorine. The difference is large for aliphatic and aliphatic–aromatic (*e.g.* toluene) solvents, whilst for aromatic solvents (*e.g.* benzene, chlorobenzene) it is almost zero. A general feature is an increase in quantum yields of both processes with increasing energy of photons of the active radiation and of the $PbCl_4$ concentration in solution.

The quantum yields φ_{Pb} [12] for the loss of $PbCl_4$ increase in the following sequence: $C_6H_5Cl < CCl_4 < C_6H_6 < CHCl_3 < C_6H_5CH_3 < C_6H_{12}$. However, the φ_{ox} values increase as follows: CCl_4 ($\varphi_{ox} = 0$) $< C_5H_5N < C_6H_5Cl < CHCl_3 < DMF < C_6H_6 < C_6H_5CH_3 < C_6H_{12}$. Consequently chlorinated solvents or those forming relatively stable complexes with $PbCl_4$ [8, 10] undergo chlorination most reluctantly. In contrast, aliphatic or aliphatic–aromatic hydrocarbons are readily chlorinated. Moreover, in systems in which $PbCl_2$ is precipitated ($PbCl_4$–$CHCl_3$, $PbCl_4$–cyclohexane) the losses of $PbCl_4$ and of oxidants continue to increase with time after pulse irradiation (Tables 2 and 3). It has also been observed that the concentration of $PbCl_4$ in irradiated solutions drops more rapidly than that of the oxidants. Accordingly, the losses of $PbCl_4$ expressed in molar terms are greater than those of the oxidants. When the $PbCl_2$ crystals are removed after irradiation by centrifugation both effects are observed, the losses being smaller than those in the presence of $PbCl_2$ (*cf.* the systems $PbCl_4$–cyclohexane and $PbCl_4$–$CHCl_3$ in Table 3). These changes were not observed in DMF in which $PbCl_2$ is soluble.

In all systems the photochemical reaction products include $PbCl_2$, Cl_2 and compounds arising from chlorination of components of a given system. The latter could not be identified in all systems. However, in those in which they were detected, they were the main products of the photochemical reaction complementing almost the whole loss of the oxidants.

Complementary information has been obtained from the pulse photolysis of chlorine solutions. The results are shown in Table 4. As seen, quantum yields for the loss of chlorine are almost 20-fold higher than those

TABLE 2

The losses of $PbCl_4$ (n_{Pb}) and of total oxidants (n_{ox}) in cyclohexane solutions measured immediately after (superscript zero) and 20 min after (superscript 20) the flash

Concentration of $PbCl_4$ $C^0_{Pb} \times 10^3$ (M)	$n^0_{Pb} \times 10^6$ (mole)	$n^{20}_{Pb} \times 10^6$ (mole)	$n^0_{ox} \times 10^6$ (mole)	$n^{20}_{ox} \times 10^6$ (mole)	$(n^{20}_{Pb} - n^0_{Pb}) \times 10^6$ (mole)	$(n^{20}_{ox} - n^0_{ox}) \times 10^6$ (mole)
0.58_2	$13._3$	$15._4$	9.8_9	$11._7$	2.1	1.8
1.9_4	$21._9$	$28._3$	$18._3$	—	6.4	—
4.05	$32._5$	$47._6$	$24._4$	$30._7$	15.0	6.3
6.15	$37._8$	$58._4$	$28._0$	$37._2$	20	9.2

of the oxidants in appropriate $PbCl_4$ solutions. Moreover, the composition of photochlorination products of the solvents is entirely different in both cases. It is worth noting that the photochemical reaction of chlorine in benzene solutions does not yield chlorobenzene as does that in $PbCl_4$ solutions.

TABLE 3

Loss of total oxidants measured at various intervals after flash

System	Time (min)	Concentration of oxidants in solutions ($\times 10^3$)		Oxidants loss ($\times 10^6$ mole)
		Non-irradiated (M)	Irradiated (M)	
$PbCl_4$-cyclohexane[a]	1.5	2.2_7	1.7_3	$13._4$
	20	2.2_6	1.6_5	$15._4$
	40	2.2_5	1.6_2	$15._7$
	80	2.1_7	1.3_2	$21._4$
$PbCl_4$-$CHCl_3$[b]	1.5	3.4_8	3.4_0	1.8_0
	20	3.4_7	3.3_4	3.1_4
	40	3.4_5	3.2_3	5.3_9
	80	3.4_1	3.0_6	8.7_6
$PbCl_4$-DMF[c]	1.5	3.8_2	3.6_1	5.1_7
	20	3.8_2	3.6_1	5.1_7
	40	3.8_2	3.6_1	5.1_7
	80	3.8_0	3.6_0	4.9_4

[a] Filterless irradiation was used; after pulse irradiation the solutions were centrifuged for 5 min and then analysed.
[b] Irradiation with 1 cm layer of $CHCl_3$ as a filter was employed; the solutions were not centrifuged.
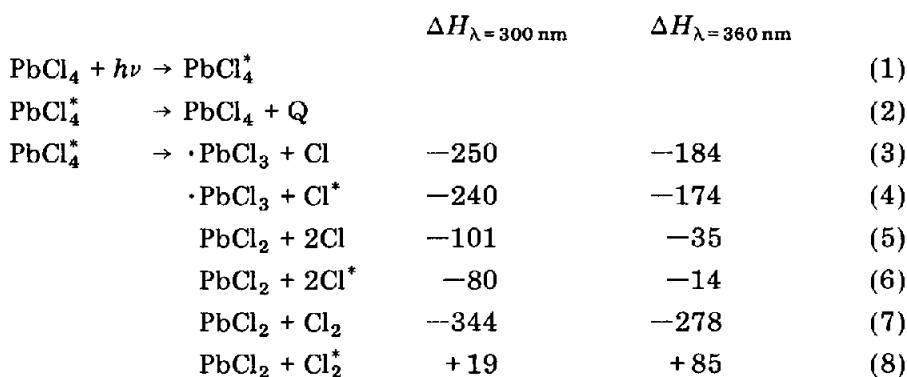[c] Irradiation with 1 cm layer of DMF as a filter was employed.

4. Discussion

A long wavelength absorption band of $PbCl_4$ around 290 nm in solutions in which EDA interactions are absent [11] may be due to the $n_{Cl} \rightarrow \sigma^*_{Pb-Cl}$ transition by analogy with absorption bands of chloromethanes [21]. The σ^*_{Pb-Cl} state should provide a dissociative state with an expected unitary quantum yield of the primary process. An alternative and more probable electron transfer, which was suggested by us earlier [6], is that of lone electrons of the chlorine atoms into an unoccupied orbital of the lead atom (LMCT). In this case the absorption leads instead to binding states of the molecule and its dissociation should occur in another electronic state, e.g. σ^*_{Pb-Cl}, i.e. it should be of the predissociation type. In the latter case we must also take into account the possibility of conversion of the electronic

TABLE 4

Results of pulse photolysis of the chlorine solutions in cyclohexane and benzene

Solvent	λ_{max} (nm)	Quantum efficiency of chlorine consumption (mole einstein^{-1})	Organic products	Yield (mole n_{ox}^{-1})
Cyclohexane	360	21.8	chlorocyclohexane	90.3
			1,2-*trans*-dichlorocyclohexane dicyclohexyl	formed in traces in 1:1 ratio
	300	29.4	chlorocyclohexane	87.8
			1,2-*trans*-dichlorocyclohexane dicyclohexyl	formed in traces in 1:1 ratio
Benzene	360	6.0	chlorobenzene	traces
	300	9.0		

energy to vibrational energy followed by dissociation of the vibrationally excited molecule which has been shown to be thermodynamically unstable [1]. Absorption via LMCT is not necessarily accompanied by a unitary quantum yield of the primary process.

Taking into account the preceding considerations, the following equations can be suggested as a description of primary processes occurring in solvents which are neutral with respect to EDA interactions:
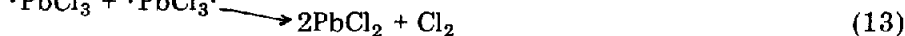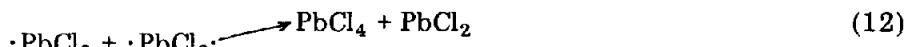
		$\Delta H_{\lambda = 300\,nm}$	$\Delta H_{\lambda = 360\,nm}$	
$PbCl_4 + h\nu \rightarrow PbCl_4^*$				(1)
$PbCl_4^*$	$\rightarrow PbCl_4 + Q$			(2)
$PbCl_4^*$	$\rightarrow \cdot PbCl_3 + Cl$	-250	-184	(3)
	$\cdot PbCl_3 + Cl^*$	-240	-174	(4)
	$PbCl_2 + 2Cl$	-101	-35	(5)
	$PbCl_2 + 2Cl^*$	-80	-14	(6)
	$PbCl_2 + Cl_2$	-344	-278	(7)
	$PbCl_2 + Cl_2^*$	$+19$	$+85$	(8)

The ΔH values for the two wavelengths were calculated using the Hess equation, assuming the Pb—Cl bond energies in the $PbCl_4$ and $PbCl_2$ molecules to be equal and amounting to 149 kJ mol^{-1} [1] and neglecting an increase in this energy on going from $PbCl_4$ to $PbCl_2$. The energy of chlorine atoms in the electronically excited state $3^2P_{1/2}$ was assumed to be 10.5 kJ mol^{-1}, the dissociation energy of Cl_2 molecules 243 kJ mol^{-1} and the electronic energy of the Cl_2 molecule in the excited state $^1\Pi_{1u}$ 363 kJ mol^{-1}. The calculated ΔH values provide a rough estimate of the excess of energy carried by fragments following dissociation.
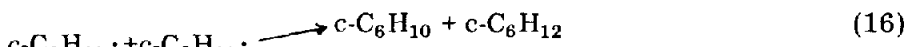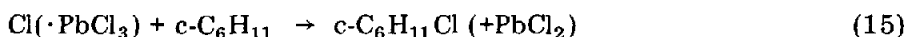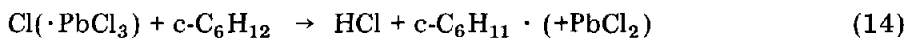
The course of the primary process, described by eqns. (5) and (6), appears to be improbable, particularly in the low energy region of incident radiation. The irradiation of $PbCl_4$ solutions is known to induce photo-chemical reactions. Accordingly, in the primary process reactive species such as $\cdot PbCl_3$, Cl, Cl^* and Cl_2^* should be formed. The non-excited chlorine molecules do not react under these conditions, as has been shown experimentally. Hence, the contribution of reaction (7) cannot be dominant. Reaction (8) does not appear to be thermodynamically possible and moreover results of irradiation of chlorine and $PbCl_4$ in two selected solvents were entirely different. Consequently, reactions (3) and (4) appear to be the most probable primary processes. The differences in the energy of chlorine atoms in the ground state $3^2P_{3/2}$ and in the excited state $3^2P_{1/2}$ are small and hence the reactivities of the states can be assumed to be roughly equal. Bearing this in mind, further pathways of the secondary processes have been suggested based on reaction (3) as the primary process.

The absorption of radiation by chlorine molecules over the $^1\Pi_{1u} \leftarrow {}^1\Sigma_g^+$ transition range has been described in detail [22] and photodissociation of the molecule affords two chlorine atoms in the ground state.

In the CCl_4 solutions secondary processes occurring with participation of fragments of the photolysis of $PbCl_4$ probably follow a similar pattern to those occurring with continuous irradiation:
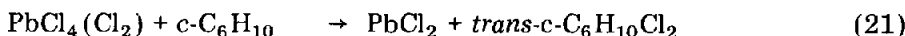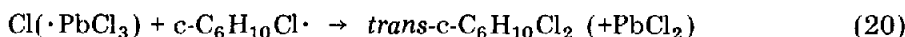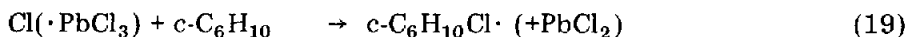
$$Cl + Cl \rightarrow Cl_2 \tag{9}$$

$$Cl + \cdot PbCl_3 \begin{cases} \nearrow PbCl_4 & (10) \\ \searrow PbCl_2 + Cl_2 & (11) \end{cases}$$

$$\cdot PbCl_3 + \cdot PbCl_3 \cdot \begin{cases} \nearrow PbCl_4 + PbCl_2 & (12) \\ \searrow 2PbCl_2 + Cl_2 & (13) \end{cases}$$

In contrast, in the cyclohexane solutions, in addition to reactions (9) - (13), those between the fragments of photolysis of $PbCl_4$ or Cl_2 and the solvent are also possible:

$$Cl(\cdot PbCl_3) + c\text{-}C_6H_{12} \rightarrow HCl + c\text{-}C_6H_{11} \cdot (+PbCl_2) \tag{14}$$

$$Cl(\cdot PbCl_3) + c\text{-}C_6H_{11} \rightarrow c\text{-}C_6H_{11}Cl (+PbCl_2) \tag{15}$$

$$c\text{-}C_6H_{11} \cdot + c\text{-}C_6H_{11} \cdot \begin{cases} \nearrow c\text{-}C_6H_{10} + c\text{-}C_6H_{12} & (16) \\ \searrow C_{12}H_{22} & (17) \end{cases}$$

Quantum yields for the photolysis of $PbCl_4$ exceeding unity can arise from contribution from chain processes, *e.g.*

$$PbCl_4(Cl_2) + c\text{-}C_6H_{11} \cdot \rightarrow \cdot PbCl_3(Cl) + c\text{-}C_6H_{11}Cl \tag{18}$$
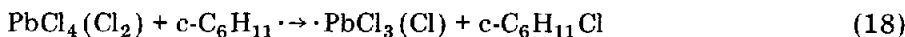
1,2-*trans*-dichlorocyclohexane can arise from the reactions

$$Cl(\cdot PbCl_3) + c\text{-}C_6H_{10} \rightarrow c\text{-}C_6H_{10}Cl \cdot (+PbCl_2) \tag{19}$$

$$Cl(\cdot PbCl_3) + c\text{-}C_6H_{10}Cl \cdot \rightarrow trans\text{-}c\text{-}C_6H_{10}Cl_2 (+PbCl_2) \tag{20}$$

$$PbCl_4(Cl_2) + c\text{-}C_6H_{10} \rightarrow PbCl_2 + trans\text{-}c\text{-}C_6H_{10}Cl_2 \tag{21}$$

Chlorocyclohexane is the main product because reactions (14), (15) and (18) are much faster than reactions (16) and (17). Reaction (14), which involves chlorine atoms, occurs in the liquid phase with a low activation energy of 6.3 kJ mol^{-1} [23]. It is worth noting that the rate constants of reactions (16) and (17) in the gas phase (384 - 475 K) are of the order of 10^7 dm^3 mol^{-1} s^{-1} [24] which are a few orders of magnitude smaller than those reported for abstraction of hydrogen atoms from hydrocarbon molecules by chlorine atoms (*e.g.* for the reaction $Cl + C_2H_6 \rightarrow HCl + \cdot C_2H_5$ in the gas phase the rate constant k has the value $(7.29 \pm 1.23) \times 10^{-11} \times \exp\{-(121 \pm 87/RT)\}$ dm^3 $molecule^{-1}$ s^{-1} [25], where $R = 1.98$ cal mol^{-1} K^{-1}). The reaction products should also contain cyclohexene and bicyclohexyl in comparable quantities since the ratio $k_{disproportionation}/k_{recombination}$ of cyclohexyl radicals equals 1.1 in the liquid phase, as has been reported by Cramer [26]. Cyclohexene has not been detected among the products.

Probably it participates in further transformations to produce 1,2-*trans*-dichlorocyclohexane (reactions (18) - (21)). These reactions are rapid, *e.g.* the activation energy for the addition of chlorine to a double bond has been reported to be close to zero [23]. Addition of chlorine atoms to a double bond should occur in axial positions by analogy with for example photochemically induced reactions of bromine with cyclohexene [27]. This has also been supported by theoretical calculations [28]. The preparation and use of cyclohexane free of detectable quantities of cyclohexene enabled us to draw the conclusion that during the photochemical reaction in the system $PbCl_4$–cyclohexane the quantity of 1,2-*trans*-dichlorocyclohexane is almost 20 times greater than that of bicyclohexyl. Probably there is an alternative pathway leading to cyclohexene, *e.g.* the reaction

$$\text{c-}C_6H_{11}\cdot + \cdot PbCl_3 \rightarrow HCl + PbCl_2 + \text{c-}C_6H_{10} \tag{22}$$
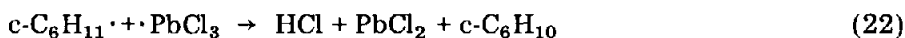
An almost 20-fold higher quantum yield for the formation of chlorocyclohexane in photochemical reactions of cyclohexane with chlorine, as compared with that of cyclohexane with $PbCl_4$, supports our earlier hypothesis about the predissociative nature of the primary process in the latter reaction. In contrast, the yields of secondary processes in the two systems would not differ so much.

Photochemical reactions of $PbCl_4$ in aromatic hydrocarbons should follow another pathway because at a large excess of the donor the radiation is absorbed mainly by the EDA complexes occurring in the ground state. Accordingly, the primary process can be described as follows:

$$ArH\cdots PbCl_4 + h\nu_{CT} \rightarrow (Ar\dot{H}^+\cdots PbCl_4^-\cdot)^* \tag{23}$$
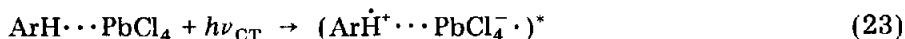
Further transformations can occur within the exciplex, as during continuous irradiation [6], and yield $PbCl_2$, HCl and products of the solvent chlorination:

$$(Ar\dot{H}^+\cdots PbCl_4^-\cdot)^* \rightarrow PbCl_2 + (ArHCl)^* + Cl^- \tag{24}$$

$$(ArHCl)^+ \rightarrow ArCl + H^+ \tag{25}$$
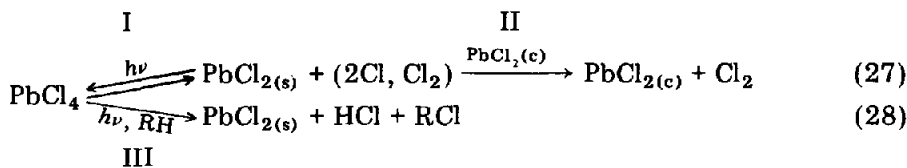
$$H^+ + Cl^- \rightarrow HCl \tag{26}$$

The formation of particular products of the photochemical reaction can be explained using resonance structures of the suggested radical cation $Ar^{+\cdot}$. As has been demonstrated experimentally, these structures favour the formation of the *ortho* and *para* isomers of dichlorobenzene and chlorotoluene. Toluene provides a slightly different case. As the compound possesses an aliphatic substituent, measured quantum yields are much higher than those of the two remaining aromatic solvents. Upon dilution of the system with CCl_4, the percentage of products of chlorination of the methyl group increases. This is indicative of a dual mechanism of the reaction in this system: (1) a radical mechanism analogous to that suggested for the cyclohexane solutions and for photochemically induced reactions of CCl_4 in toluene [29]; (2) a mechanism requiring electron transfer in the primary

process followed by rearrangements within the exciplex formed. Upon dilution of the system with CCl_4 the first mechanism predominates, whilst in the pure toluene the reaction follows mainly the second route.
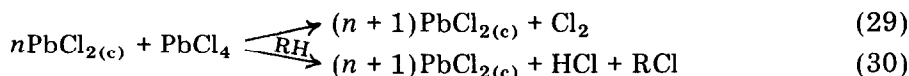
Chlorine dissolved in benzene is bound almost completely into a complex (stability constant $K_c = 0.35$ [30]), as is $PbCl_4$. This is reflected by the disappearance of the 330 nm band in the UV spectrum. Consequently, the primary process should be analogous to reaction (23). However, reactions within the exciplex must be dissimilar to those in the case of $PbCl_4$ because entirely different products are formed.

A crucial point provides a comparison of results obtained earlier during continuous irradiations [4 - 12] with those obtained by the pulse technique [12]. Despite many similar features there are, however, essential differences. All quantum yields for pulse irradiation have been found to be a few times lower than those for continuous irradiation. The contribution of the reaction of solvent chlorination (φ_{ox}) to the overall loss of reactant (φ_{Pb}) is dominant in pulse irradiation, whereas under continuous irradiation the photolysis of $PbCl_4$ provides the main process (i.e. the difference $\varphi_{Pb} - \varphi_{ox}$ is large). Furthermore there are occasional differences in the products of photochlorination of the solvent. For instance with chlorobenzene pulse irradiation yields p-dichlorobenzene along with o-dichlorobenzene, the latter being the sole photoproduct with continuous irradiation; with toluene the ratio of the quantities of isomers formed reveals a clear-cut dominance of chlorination of the methyl group during pulse irradiation, whereas during continuous irradiation only products of chlorination of the aromatic ring arise, as was the case with thermal reactions [6]. There are at least two reasons for these differences. In all solvents except for pyridine and DMF solid $PbCl_2$ ($PbCl_{2(c)}$) provides a thermodynamically stable phase. Taking into account experimental conditions, we can assume that the $PbCl_2$ crystals are formed over considerably longer periods than the pulse duration. The rate of the process depends, among others, on the following parameters: the diffusion coefficient of $PbCl_2$ molecules in solution ($PbCl_{2(s)}$), the temperature, the nature of the solvent, the concentration of $PbCl_{2(s)}$ and the presence of crystallization nuclei. The last two factors are entirely different for pulse and continuous irradiation conditions. If the overall process occurring in the systems is described by the equations

$$
\begin{array}{ccc}
& \text{I} & \text{II} \\
PbCl_4 & \underset{\xrightarrow{h\nu,\ RH}}{\overset{h\nu}{\rightleftarrows}} PbCl_{2(s)} + (2Cl,\ Cl_2) \xrightarrow{PbCl_{2}(c)} PbCl_{2(c)} + Cl_2 & (27) \\
& \xrightarrow{} PbCl_{2(s)} + HCl + RCl & (28) \\
& \text{III} &
\end{array}
$$

the reversible reaction (I) will be much faster in the back direction during pulse photolysis owing to the much higher (by a few orders of magnitude) $PbCl_{2(s)}$ concentration and the absence of crystallization nuclei. For the same reason the contribution of recombination reactions of the type (10) should be much higher in the pulse technique.

The second reason for the differences is that during pulse irradiation products of the photochemical process can be obtained under conditions in which thermal processes are eliminated after irradiation by removing $PbCl_4$ and Cl_2. In contrast, during prolonged steady irradiation photochemical processes are accompanied by thermal ones, the latter being markedly accelerated (photoinduced) by a fresh highly dispersed phase of the solid $PbCl_2$. Consequently, during continuous irradiation unexpectedly high quantum yields are obtained as well as products resulting from both photochemical and photoinduced processes. The comparative method employed for the present cases does not rule out the contribution of thermal reactions owing to the phenomenon of their photoinduction. During continuous irradiation this photoinduction can give rise to a considerably higher contribution of $PbCl_4$ to $PbCl_2$ and Cl_2 to total loss of $PbCl_4$. The data of Table 3 demonstrate convincingly that the ratio $\varphi_{ox}/\varphi_{Pb}$ decreases with time after pulse irradiation. Photoinduced reactions are mostly decomposition processes of $PbCl_4$ and to a smaller extent those of chlorination of the solvent. The course of the photoinduced processes can be schematically described as follows:

$$nPbCl_{2(c)} + PbCl_4 \xrightarrow{\hspace{1cm}} (n + 1)PbCl_{2(c)} + Cl_2 \tag{29}$$
$$\xrightarrow{RH} (n + 1)PbCl_{2(c)} + HCl + RCl \tag{30}$$

These processes only occur to a small extent in pulse photolysis; hence the $\varphi_{ox}/\varphi_{Pb}$ ratio is close to unity.

Acknowledgments

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