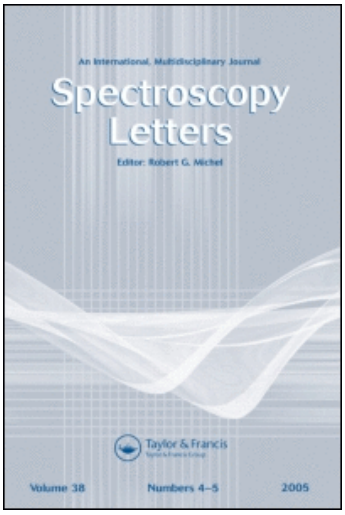

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Yong Yu[a]; Shuhui Wang[a]; Xian-Nian Liu[a]; Jian Hou[a]; Hui-Qi Hou[a]; Side Yao[b]; Wenfeng Wang[b]
[a] Institute of Environmental Science, Fudan University, Shanghai, China [b] Laboratory of Radiation Chemistry, Chinese Academy of Science, Shanghai, China

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THE NANOSECOND LASER FLASH PHOTOLYSIS (LFP) TRANSIENT SPECTRA OF AQUEOUS CCL_4 SOLUTION

Keywords: transient spectra; aqueous CCl_4 solution; laser flash photolysis

Yong Yu, Shuhui Wang, Xian-nian Liu, Jian Hou, Hui-qi Hou
Institute of Environmental Science, Fudan University, Shanghai 200433, China
Side Yao, Wenfeng Wang
Laboratory of Radiation Chemistry, Chinese Academy of Science, P.O.Box 800-204, Shanghai 201800, China

ABSTRACT

The transient spectra of aqueous CCl_4 solution by laser flash photolysis (LFP) was studied in this paper. The transient absorption band (λ_{max} <300nm) of aqueous CCl_4 solution bubbled with N_2 was attributed to the trichloromethyl radical ($CCl_3^{\bullet}$) with a 2rd-order decayed reaction rate of $3.80 \times 10^8 mol^{-1} \bullet L \bullet s^{-1}$. The transient absorption band (λ_{max} 320nm) of the same solution bubbled with O_2 was attributed to the peroxytrichloromethyl radical ($CCl_3O_2^{\bullet}$) with a 1st-order decay reaction rate of $1.9 \times 10^4 s^{-1}$. The transient absorption band around 330 nm of aqueous CCl_4 solution always exists insolutions bubbled with either N_2 or O_2 and was attributed to the solvated chlorine atom (Cl). $COCl_2$ as a photolysis product of aqueous CCl_4 solution, in the presence of O_2 , was observed directly in the transient absorption spectra. The results indicate that CCl_4 can be degraded by the photooxidation process.

INTRODUCTION

There is widespread and growing concern over the environmental and health impact of chlorinated organic compounds. UV-Photooxidation (with dissolved oxygen in solution) is the cheaper and more effective method of inducing degradation processes for chlorinated organic compounds. A question arises as to the effectiveness of UV-Photooxidation (with dissolved oxygen in solution) specifically for chlorinated aliphatic compounds. The answer is uncertain because the mechanism of dechlorination has been not yet been fully delineated[1]. The Laser Flash Photolysis (LFP) technique is a useful method to study fast processes and reaction mechanisms of photochemistry. The LFP technique is useful to study dechlorination and free radical oxidation mechanisms of irradiation processes in aqueous systems containing chlorinated organic compounds. In our experiment, we used the nanosecond Laser Flash Photolysis (LFP) technique to study the transient spectra of aqueous CCl_4 that indicates its dechlorination mechanism. This paper will describe the transient spectra and some aspects of the elementary reactions of transient species formed in the 248 nm laser pulse in aqueous CCl_4 solution. We have found direct evidence that CCl_4 can be degraded by this photooxidation process.

EXPERIMENTAL DETAILS

CCl_4 was purified by the addition of concentrated KOH three times at 50°C and then rinsed three times by water. After that, CCl_4 was washed using high purity H_2O five times and then rinsed additionally several times. CCl_4 was dried over $CaCl_2$ and then distilled. The aqueous CCl_4 solution was prepared by using triply distilled water or 5N distilled tertabutyl alcohol (tert-BuOH) solution. A quartz cell (1 cm by 1 cm inner dimensions) was used as the sample cell. All Samples were further treated by bubbling high purity nitrogen (99.99%) or high purity oxygen (99.5%) for 30 min before doing experiments. All experiments were done at room temperature (25 °C).

A homemade KrF excimer laser provided a 248 nm light pulse with duration of 20 ns in the laser flash photolysis experiments. The maximum laser energy was 40 mJ per pulse. The signal was detected using a HP54510B 300 MHz transient recorder and then processed with a PC-486 computer. Experimental details are given elsewhere[2].

RESULTS AND DISCUSSION

1 Transient Absorption Spectra of Aqueous CCl_4 Solution

In the transient absorption spectra of aqueous CCl_4 solution bubbled with nitrogen or oxygen, there is no evident absorption band beyond 400 nm, indicating no aqueous electrons have formed. The photo-excition process of CCl_4 is a one-photon process. The primary photochemical process in aqueous CCl_4 solution excited by the 248 nm laser light can be described as follows:

$$CCl_4 + h\nu \rightarrow CCl_4^{\bullet} \rightarrow CCl_3^{\bullet} + Cl^{\bullet} \qquad (1)$$

1.1 Aqueous CCl4 solution bubbled by nitrogen

Fig.1 shows that one obvious absorption band is found around 330 nm at 0.1 μs after laser the pulse. The absorption band around 330 nm is attributed to the solvated chlorine atom because there were no reports about the trichloromethyl radical ($CCl_3^{\bullet}$) and pure chlorine atom (not solvated chlorine atom) having a transient absorption band around 330 nm until now. Treinin and his co-worker [3] obtained the transient spectra of chlorine atoms in water by photolysis of chlorine in water. They attributed the transient species with an absorption band around 320nm to charge-transfer(CT) transition from a water molecule to a chlorine atom. In fact, the solvated chlorine atom in our study and charge-transfer(CT) transition from a water molecule to a chlorine atom in Treinin's experiment is the same species.

The formation and decay trajectories at 330 nm and 380 nm (Fig.2) shows that there is a quite difference between curve 1 for 330 nm and curve 2 for 380 nm in Fig.2. The transient species at 380 nm formed immediately after the laser pulse and decayed in several μs. The decay rate of transient species at 380 nm is a 1st-order reaction with rate constant 2.0×10^{-5} s^{-1}. However, there is a stable absorption at 330 nm after 5μs. It can be explained that two species exist at 330 nm absorption. Curve 3 corresponding to the formation and decay trajectory of stable species was obtained by subtracting pA^{380nm} from A^{330nm}[2]. Treinin [3] and Ulrik[4] reported that observation of the Cl atom was possible in acid solution owing to hydrolysis of the chlorine atom in water. It means that the solvated chlorine atom is not a stable species and it can form the other species by hydrolysis. Then the reaction of the chlorine atom after primary photochemical process can be described as follows:

$$Cl^{\bullet} + H_2O \rightarrow \{Cl\}_{sol} \rightarrow ClOH^{-} + H^{+} \qquad (2)\ k_2$$

We attribute the other transient species at 330nm to $ClOH^{-}$ which has an absorption band around 320 nm. Curve2 and curve 3 in Fig.2 show a good correlation between decay of $\{Cl\}_{sol}$ and formation of $ClOH^{-}$. It reflects that the reaction mechanism we supposed is reasonable. From our calculation, the lifetime of the solvated chlorine atom is 3.5μs.

Lesighe and his co-worker reported the trichloromethyl radical ($CCl_3^{\bullet}$) had a transient absorption band < 300 nm using pulse radiolysis of aqueous CCl_4 solution [5]. But in our experiment results, there is no evident transient absorption bands < 300 nm which may be because of the lower concentration of CCl_4 in solution. When we increase the concentration of CCl_4 in solution, there is an evident transient spectra of trichloromethyl radical which will be discussed later.

1.2 Aqueous CCl_4 solution bubbled by oxygen

The transient absorption spectra of aqueous CCl_4 solution bubbled by oxygen recorded at different times is the same as aqueous CCl_4 solution bubbled using

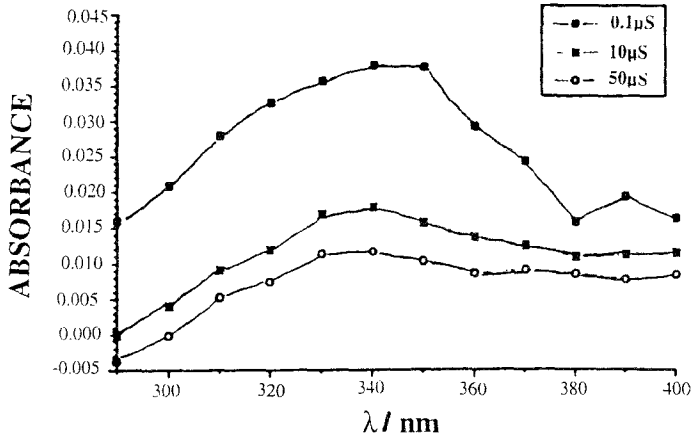

Fig.1 Transient absorption spectra of aqueous CCl_4 solution after laser photolysis

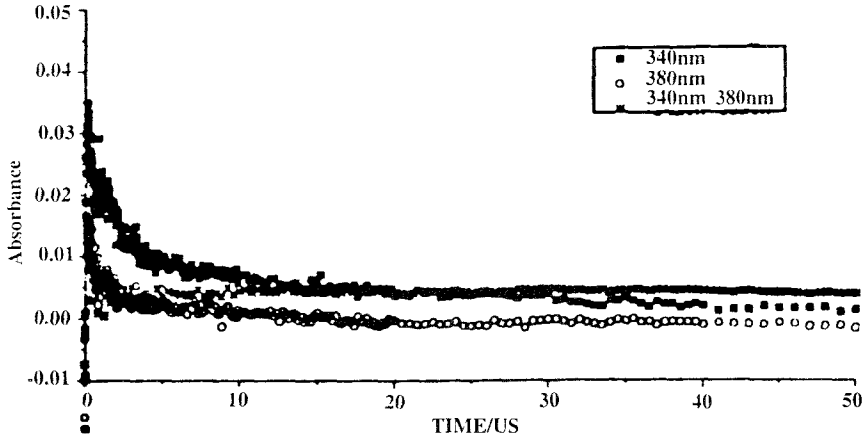

Fig.2 Transient formation and decay trajectories of aqueous CCl_4 solution saturated with nitrogen

nitrogen. So we can conclude the oxygen has no effect on chlorine atom solvation and the solvated chlorine atom reaction. In our experiment, there is no evident transient absorption spectra of the trichloromethyldioxy free radical ($CCl_3O_2^{\bullet}$) for the lower CCl_4 concentration in the solution, although it is possible the trichloromethyl radical can react with oxygen to form the trichloromethyldioxy free radical[6].

2 Transient Absorption Spectra of Aqueous CCl_4 Solution Contained Tertabutyl Alcohol (tert-BuOH)

2.1 Aqueous CCl_4 solution containing tert-BuOH bubbled by nitrogen

The transient absorption spectra were observed at various times as shown in Fig.3 from laser flash photolysis of 4% CCl_4 in aqueous tert-BuOH solution. There is only one absorption band ($\lambda_{max} < 280$nm) as shown in Fig.3, at 0.1 μs after the laser pulse. In the transient absorption spectra, there are no obvious absorption bands > 400nm indicating that no aqueous electrons are formed. The photo-excition process of CCl_4 is a one -photon process too. As the mechanism mentioned before, the solvated chlorine atom could be formed after the laser pulse, but in our experiment, no evident absorption spectra were observed for following reaction:

$$Cl^{\bullet} + \text{tert-BuOH} \rightarrow HCl + (CH_3)_2COH\,CH_2^{\bullet} \qquad (3)\ k_3$$

Due to two competitive reactions (reaction 2 and reaction 3), we obtain:

$$-\frac{d[Cl^{\bullet}]}{dt} = k_2[Cl^{\bullet}][H_2O] + k_3[Cl^{\bullet}][tert-BuOH] = (k_2[H_2O] + k_3[tert-BuOH])[Cl^{\bullet}]$$

For k_3[tert-BuOH]>>$k_2[H_2O]$ (where upper reaction rate constant is about 0.7~3.2 $\times 10^9$ $mol^{-1}\bullet L\bullet s^{-1}$[7-8] and the concentration of tert-BuOH in solution is about 4.76 $mol\bullet L^{-1}$). Reaction 3 is the primary process of competition between reaction 2 and reaction 3, and reaction 2 can be negligible. Once the Cl atom formed, it converted to HCl immediately and did not exhibit the same absorption spectra as the aqueous CCl_4 solution in the absence of tert-BuOH.

From the formation and decay trajectory at 270 nm (Fig.4), it shows that the transient species was produced immediately after the laser pulse and then decayed slowly. From the kinetic analysis of the transient absorption decay, the transient species can be described as a bimolecular decay. It can be deduced that the transient species with the transient absorption ($\lambda_{max} < 300$nm) is attributed to the trichloromethyl radical ($CCl_3^{\bullet}$) formed by reaction 1 during the laser pulse and disappears quickly by reaction 4.

$$CCl_4 + h\nu \rightarrow CCl_4^{*} \rightarrow CCl_3^{\bullet} + Cl^{\bullet} \qquad (1)$$

$$CCl_3^{\bullet} + CCl_3^{\bullet} \rightarrow C_2Cl_6 \qquad (4)$$

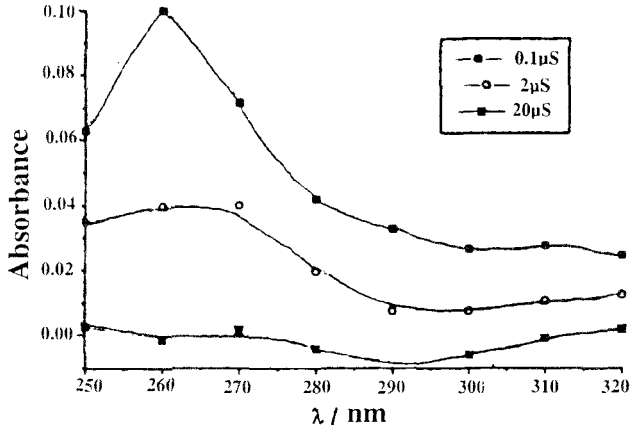

Fig.3 Transient absorption spectra of aqueous CCl_4 solution containing tert-BuOH saturated with nitrogen after laser photolysis.

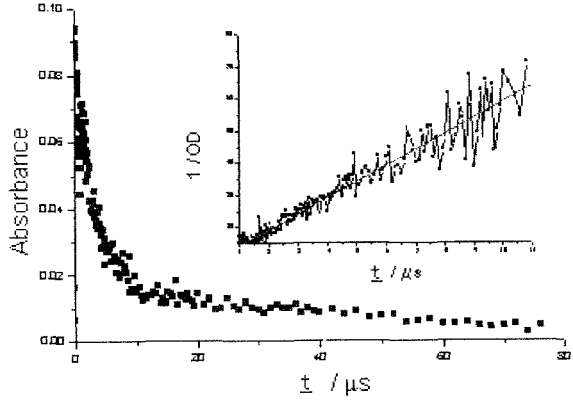

Fig.4 Transient formation and decay trajectory of aqueous CCl_4 solution containing tert-BuOH saturated with nitrogen at 270 nm. Insert: kinetic analysis of absorption decay at 270 nm.

From the 2nd - order decay plot (upper figure in Fig.4), it is straight forward to obtain the value of $(2k/\varepsilon l)$, 6.34×10^6. According to Lesighe's data (ε_{270nm})[5], the bimolecular decay reaction rate coefficient is $3.80 \times 10^8 mol^{-1}\bullet L\bullet s^{-1}$ which is in agreement with the literature[5].

2.2 Aqueous CCl_4 solution containing tert-BuOH bubbled by oxygen

Fig.5 shows the transient absorptions followed the pulse laser photolysis of aqueous CCl_4 solution containing tert-BuOH bubbled using oxygen. A longer lifetime transient species exists between 270 nm to 350 nm as shown in Fig.5. From the formation and decay trajectory at 320 nm (curve 2 in Fig. 6), it shows that the transient species formed during 0.2 μs after the laser pulse and that the decay was slower than formation. We conclude the transient species around 270-320 nm is the trichloromethyldiroxy free radical ($CCl_3O_2^\bullet$) for the following several reasons.

Reason 1: the formation and decay trajectory of the solution bubbled using oxygen at 320 nm is much different than the solution bubbled using nitrogen. This indicates the oxygen played a role in the transient species after the photolysis. As we mentioned earlier, the oxygen has no effect on the Cl atom, so the transient absorption bands at 270-350 nm may be caused by the $CCl_3O_2^\bullet$.

Reason 2: Moening [6] reported the rate constant of the $CCl_3^\bullet$ reaction with oxygen (reaction 5) is about $3.3 \times 10^9 mol^{-1}\bullet L\bullet s^{-1}$ and fordissolved oxygen in water at room temperature is $1.3 \times 10^{-3} mol\bullet L^{-1}$.

$$CCl_3^\bullet + O_2 \rightarrow CCl_3O_2^\bullet \qquad (5)$$

$$-\frac{d[CCl_3^\bullet]}{dt} = \frac{d[CCl_3O_2^\bullet]}{dt} = k_5[CCl_3^\bullet][O_2]$$

So the $CCl_3O_2^\bullet$ is formed in 0.2 μs according to experimental result.

Reason 3: Shen [9] reported the rate constant of the $CCl_3O_2^\bullet$ decay reaction is about $3.0 \times 10^4 s^{-1}$. After analysis of the absorption at 320 nm, it can be seen that the transient species decay is a 1st - order reaction and its rate constant is $1.9 \times 10^4 s^{-1}$ which is in accord with Shen's data. From our experiment, the lifetime of $CCl_3O_2^\bullet$ is obtained as 36.5 μs.

Fig.5 shows the decay of the absorbance at 300-350 nm approaching zero, but there is still a stable absorbance under 300 nm after 20 μs. These are 1st - order decay reactions with the different decay rate coefficient at 320 nm (curve 1 in Fig.6) and 280 nm (curve 2 in Fig.6), indicating that a new transient species exists under 300 nm. Curve 3 in Fig.6, corresponding to the formation and decay trajectory of stable species with time, is obtained by subtracting pA^{300nm} from A^{280nm}. Curve 1 and curve 3 in Fig.6 show that there is good correlation between the decay of $CCl_3O_2^\bullet$ and the formation of new species. We attribute the new transient species under 300 nm to $COCl_2$ for the following several reasons.

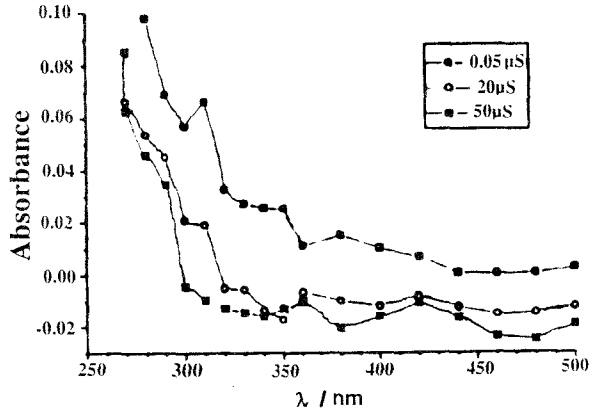

Fig.5 Transient absorption spectra of aqueous CCl_4 solution containing tert-BuOH saturated with O_2

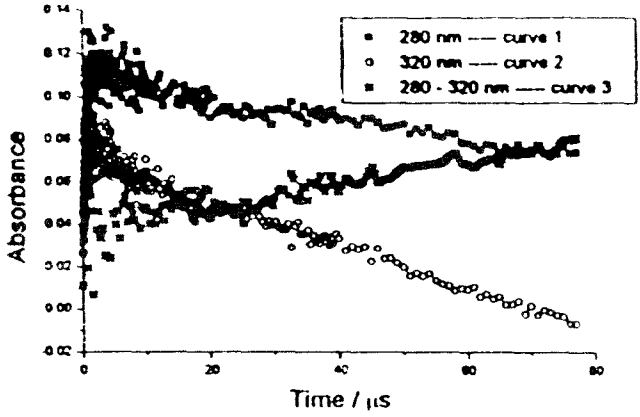

Fig.6 Transient formation and decay trajectories of aqueous CCl_4 solution containing tert-BuOH saturated with O_2

Reason 1: this new species has a UV absorption band under 300nm.
Reason 2: it is stable.
Reason 3: its formation correlates to the decay of $CCl_3O_2^{\bullet}$.

$$CCl_3O_2^{\bullet} \rightarrow COCl_2 + \ldots \quad (6)$$

Abramson reported that they find the $COCl_2$ as the product of pulse radiolysis of CCl_4 bubbled using oxygen [10], but Packer and his co-worker reported that they never found that reaction 5 occurred in same system [11].

CONCLUSIONS

The transient absorption spectra of several free radicals produced by photolysis of CCl_4 in aqueous solution were observed. The decay kinetic data and lifetimes were also investigated in this paper. The final product of photolysis of CCl_4 in aqueous solution bubbled with N_2 is C_2Cl_6 which is degraded more difficultly. The final product of photolysis of CCl_4 in aqueous solution bubbled with O_2 is $COCl_2$ which can convert to CO_2 and HCl easily. We make the conclusion that the UV-photooxidation (by dissolved oxygen in the solution) may be a useful process to degrade chlorinated aliphatic compounds.

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