# Photochemistry of Herbicide 2,4,5-Trichlorophenoxyacetic Acid in Aqueous Solutions in the Presence of Cyclodextrins

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## Abstract

Photodegradation of herbicide 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) in aqueous solutions was studied by means of steady-state and nanosecond laser flash photolysis. It was demonstrated that the primary photochemical act involves one- and two-photon ionization of the herbicide and the formation of the hydrated electron/radical cation pair. In oxygen-free solutions, hydrated electron disappears due to capturing by the initial compound, whereas the radical cation gets hydrolyzed with water to form a long-living phenoxyl radical. We also studied the formation of 2,4,5-T complexes with β- and γ-cyclodextrins (2,4,5-T-β(γ)-CD) and the effect of this process on the rate of the steady-state photolysis of the herbicide.

**Key words:** photochemistry, photodegradation, herbicides, photoionization, hydrated electron, laser flash photolysis, cyclodextrins, inclusion complexes

## INTRODUCTION

2,4,5-Trichlorophenoxyacetic acid (2,4,5-T) is one of the most widely used herbicides in agriculture, whose world production amounts to dozens thousand tons per year [1, 2]. As a derivative of 2,4,5-trichlorophenol, 2,4,5-T is a toxic substance, and its delivery into water reservoirs results in the deterioration of drinking water quality [1, 3, 4]. The photochemical method is considered one of the most promising approaches to purifying water systems from toxic organic compounds [5, 6].

Cyclodextrins (CD) those represent cyclic oligosaccharides usually consist of 6(α-CD), 7(β-CD) or 8(γ-CD) molecular residues of α-*D*-glucopyranose combined into macrocycles by α-*D*-1,4-glycoside bonds. Owing to the presence of an outer hydrophilic periphery and a hydrophobic internal cavity, CD can form inclusion complexes of guest−host type with various hydrophobic compounds. As the result, the photochemistry and photophysics of the guest molecule often undergoes significant changing.

Recently it was demonstrated that the formation of such complexes could be used to develop novel catalytic methods for photochemical purification from impurities in solutions and in solid phase [7−9].

The literature reported a steady-state photolysis of aqueous solutions [2] and photocatalytic decomposition of 2,4,5-T in the presence of titanium dioxide [6, 10] to form major photodegradation products such as chlorophenols and different products resulting from the oxidation and hydrolysis of the acetyl group. No experiments with flash photolysis of 2,4,5-T were performed earlier.

This work is devoted to studying the photochemistry of 2,4,5-T in aqueous solutions using the methods of steady-state and nanosecond laser (266 nm) flash photolysis and to determining the effect of 2,4,5-T complexation with β- and γ-cyclodextrins (2,4,5-T-β(γ)-CD) on the photodegradation rate of this substance.

## EXPERIMENTAL

2,4,5-Trichlorophenoxyacetic acid (Sigma-Aldrich, >97 %), β- and γ-cyclodextrins (Wako Pure Chemical Inc., >97 %) were used without additional purification. The experiments were carried out in weakly basic aqueous solutions

(pH 9−10) within the range of acid concentration amounting to $10^{-5}-10^{-3}$ mol/L. The concentration of 2,4,5-T was determined using the extinction coefficient $\varepsilon = 2340$ $M^{-1} \cdot cm^{-1}$ ($\lambda = 289$ nm). The value of pH was measured using an Anion-4100 pH meter. The concentration range of CD amounted to $10^{-4}-10^{-2}$ mol/ L. The chemical structures of 2,4,5-T, β- and γ-CD are demonstrated in Scheme 1.

The UV absorption spectra were registered using an Agilent 8453 spectrophotometer (Agilent Technologies). For the steady-state photolysis we used a DRSh-500 medium pressure mercury lamp with water and chlorine filters for 313 and 254 nm lines. The experiments on the laser flash photolysis were conducted using
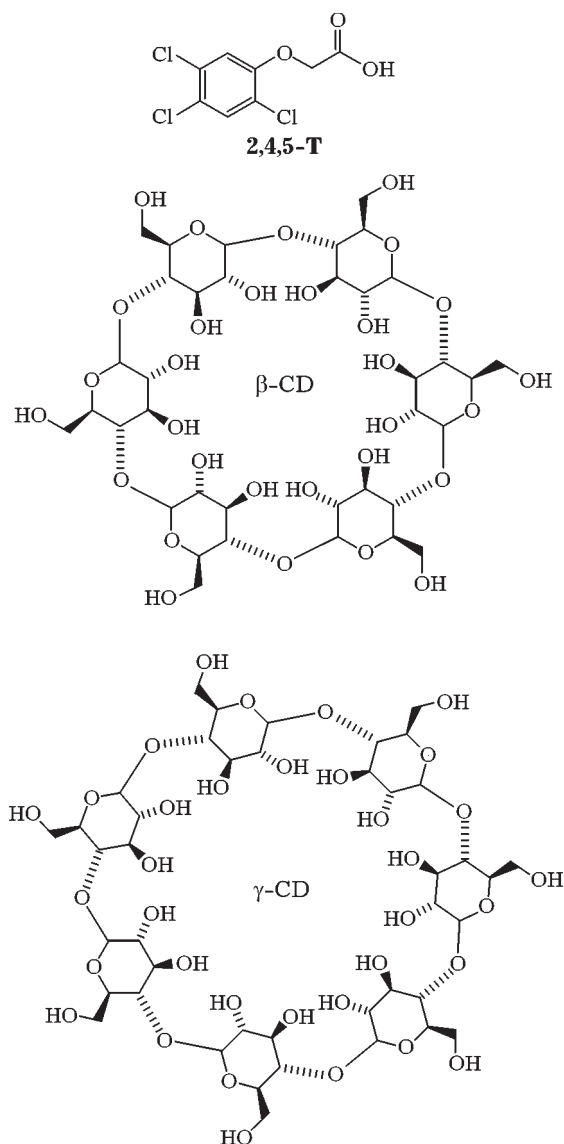
a unit described in [11], with excitation by the fourth harmonic (266 nm) of LS-2137U Nd : YAG laser (LOTIS TII) with 5−6 ns pulse duration, pulse energy ranging within 1−20 mJ). The time resolution of the unit was equal to 50 ns.

All the experiments were performed using a cell with an optical path length equal to 1 cm in oxygenated (or saturated with argon) aqueous solutions at the temperature equal to 298 K and atmospheric pressure.

## RESULTS AND DISCUSSION

### Complexation of 2,4,5-T with β- and γ-CD

Adding the cyclodextrins results in slightly changing the shape of the 2,4,5-T spectrum, which could indicate a complexation reaction to occur:

$$2,4,5\text{-T} + \text{CD} \leftrightarrow 2,4,5\text{-T−CD (complex)} \quad (1)$$
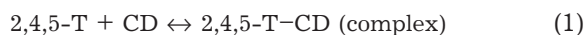
In this case there is no significant shift of the absorption band with the maximum at 289 nm (Fig. 1, *a*).
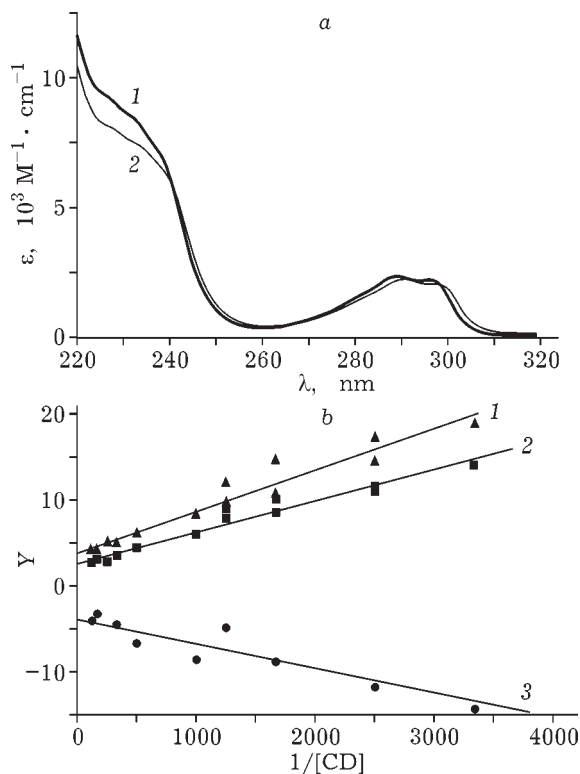
Scheme 1.

Fig. 1. Absorption spectra (*a*) and linear anamorphosis calculated *via* formula (3) at different wavelength values (*b*): *a* − 2,4,5-T (*1*), complex 2,4,5-T−β-CD (*2*); *b* − wavelength, nm: 301 (*1*), 244 (*2*) и 225 (*3*).

In order to determine the stability constant of the inclusion complex, we registered the absorption spectra of 2,4,5-T aqueous solutions under varying the concentration of CD. In the presence of CD the optical density ($A$) at an arbitrary wavelength ($\lambda$) could be expressed as

$$A^\lambda = \varepsilon_0^\lambda l\,[2,4,5\text{-T}] \;+\; \varepsilon^\lambda l[2,4,5\text{-T}-\text{CD}] \qquad (2)$$

wherein $\varepsilon_0^\lambda$ is the extinction coefficient for 2,4,5-T; $\varepsilon^\lambda$ is the extinction coefficient for complex 2,4,5-T-CD; $l$ is the optical path length, cm.

For increasing the accuracy of determining the stability constants it is appropriate to use the optical density ratio at the wavelength of measurement ($\lambda$) and at 289 nm. The reciprocal difference of these relationships ($Y$) at the current and zero concentration of CD could be written as

$$Y = c/a + b/a[\text{CD}]K_{\text{st}} \qquad (3)$$

where $\quad Y = \dfrac{A_0^{289} A^{289}}{A_0^{289} A^\lambda - A_0^\lambda A^{289}}$, $\quad a = \varepsilon_0^{289}\varepsilon^\lambda - \varepsilon_0^\lambda\varepsilon^{289}$,

$b = (\varepsilon_0^{289})^2$, $c = \varepsilon_0^{289}\varepsilon^{289}$.

Figure 1, $b$ demonstrates a linear anamorphosis in the coordinates of $Y - 1/[\text{CD}]$ for the case of $\beta$-CD with $\lambda = 225$, 244 and 301 m. One could see that at these wavelength values there is the greatest change in the optical density observed for the solutions of 2,4,5-T under complex formation. The values of stability constants for 2,4,5-T$-\beta$-CD and 2,4,5-T$-\gamma$-CD are amounting to 1100 and 150 mol/L, respectively, the extinction coefficient ($\varepsilon^{289}$) being equal to 2200 and 2100 $\text{M}^{-1}\cdot\text{cm}^{-1}$, respectively.

## Steady-state photolysis of 2,4,5-T and the complexes with CD in aqueous solutions

Figure 2, $a$ demonstrates changing the optical spectrum 2,4,5-T aqueous solution (pH 9) with under steady-state irradiation. It could be seen that the initial stage of the photolysis is characterized by the growth of absorption within the range of 245−600 nm with maxima at 260 and 500 nm and isosbestic point at 245 nm. Increasing the absorption at 500 nm stops under prolonging the irradiation exposure, which could be connected, to all appearance, with the secondary photolysis of 2,4,5-T photodegradation products (see an inset in Fig. 2, $a$).
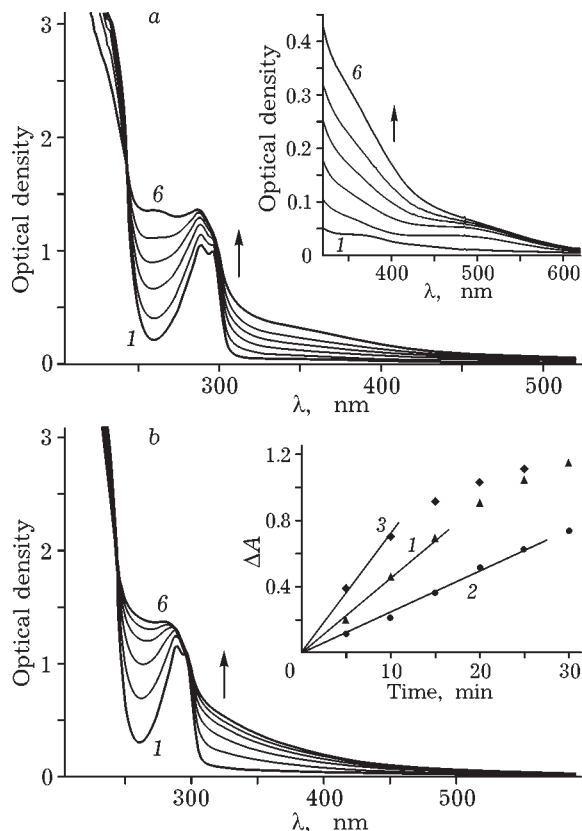


Fig. 2. Absorption spectra under steady-state 2,4,5-T photolysis, without ($a$) and with adding $\gamma$-CD ($5 \cdot 10^{-3}$ mol/L) ($b$), registration in 0 min ($1$), 5 ($2$), 10 ($3$), 15 ($4$), 20 ($5$) and 30 min ($6$) after starting the irradiation. Concentration of 2,4,5-T, mol/L: $4.4 \cdot 10^{-4}$ ($a$), $4.9 \cdot 10^{-4}$ ($b$); inset: changing the optical density at 260 nm in the course of 2,4,5-T photolysis, without ($1$) and in the presence of $\beta$-CD ($2$) and $\gamma$-CD ($3$) at the concentration equal to $5 \cdot 10^{-3}$ mol/L.

Changing the absorbance in the course of the steady-state photolysis of 2,4,5-T ($4 \cdot 10^{-4}$ mol/L) in the presence of $\gamma$-CD ($5 \cdot 10^{-3}$ mol/L, 43 % of 2,4,5-T$-\gamma$-CD complex) in an aqueous solution (pH 9) is demonstrated in Fig. 2, $b$.

It can be seen that the character of the spectral changes in the course of the photolysis does not differ from those of the uncomplexed acid, which indicates a weak influence of $\gamma$-CD upon the composition of photodegradation products. A similar situation is observed for the photolysis of 2,4,5-T ($4 \cdot 10^{-4}$ mol/L) in the presence of $\beta$-CD ($5 \cdot 10^{-3}$ M, 85 % of 2,4,5-T$-\beta$-CD complex). However, the photolysis rate calculated from the initial slope of the absorption at 260 nm plotted against the illumination depth, depends on whether cyclodextrins present in the system (see inset in Fig. 2, $b$) being 1.8 times less as compared to the rate of free acid pho-
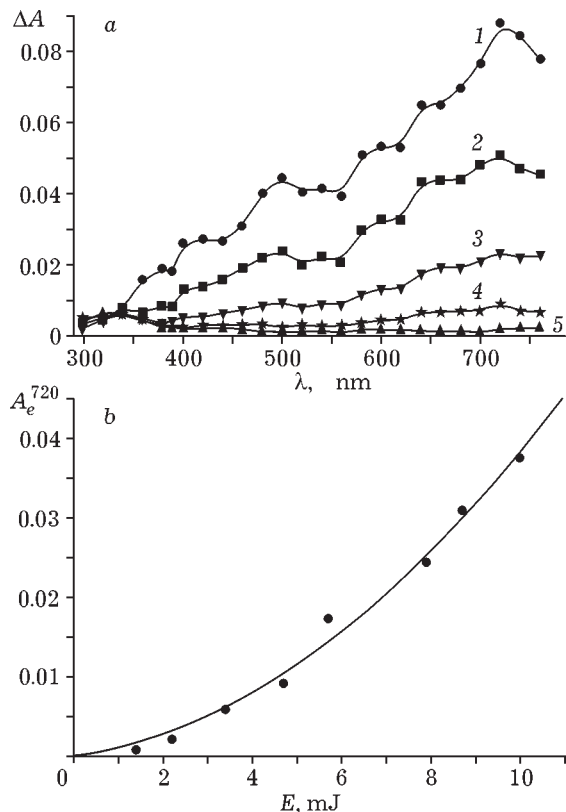
Fig. 3. Transient absorption spectra (*a*) and the initial optical absorption of hydrated electron at 720 nm ($A_e^{720}$) calculated according to the expression (5) depending on laser pulse intensity (*b*): *a* − registration after the laser excitation of 2,4,5-T ($4 \cdot 10^{-5}$ mol/L) in 0.05 µs (*1*), 0.4 (*2*), 1.6 (*3*), 4 (*4*) and 48 µs (*5*).
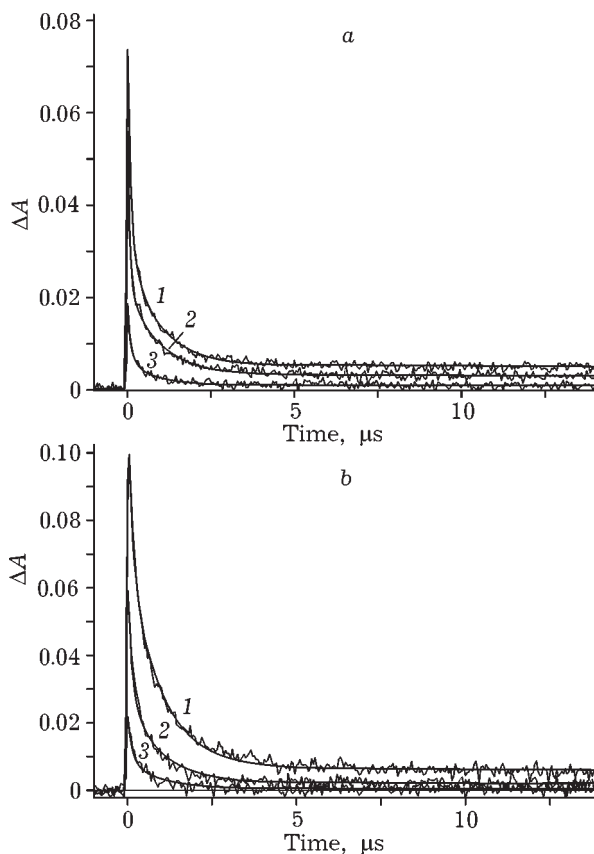


Fig. 4. Kinetic curves of absorption for disappearing the intermediate species at 480 (*a*) and 720 nm (*b*) at different initial intensity values of the excitation pulse, mJ/pulse: 9.7 (*1*), 6.5 (*2*), 4.7 (*3*); solid curves − processing according to formula (5) ($\tau_1 = 130$ ns, $\tau_2 = 1$ µs, [2,4,5-T] = $1.7 \cdot 10^{-4}$ mol/L).

tolysis the presence of β-CD and 1.5 times greater as compared to the same in the case of γ-CD used.

*Flash photolysis of 2,4,5-T*

The pulsed excitation of oxygen-free 2,4,5-T aqueous solutions (at 266 nm) results in appearing a transient absorption which consists of two bands with maxima near 500 and 720 nm (Fig. 3, *a*). The rate of disappearance for these bands differs to a considerable extent (Fig. 4), which indicates the formation of two intermediates. It is known that the broad band with a maximum at $\lambda = 720$ nm corresponds to the absorption of hydrated electron ($e_{aq}^-$, $\varepsilon^{720} = 2.27 \cdot 10^4 \, M^{-1} \cdot cm^{-1}$) [12, 13].

Thus, the UV excitation of 2,4,5-T results in photo ionization to form hydrated electron/ radical cation $[ArOAc]^{+\bullet}$ pair, which is typical for the photochemistry of chlorophenols in aqueous solutions [14−16]:

$$2,4,5\text{-T} \xrightarrow{h\nu} [ArOAc]^{+\bullet} + e_{aq}^- \qquad (4)$$

The first intermediate is characterized by an absorption band with the maximum at $\lambda = 720$ nm, the radical cation demonstrates an absorption band with the maximum at 500 nm (see Fig. 3, *a*). It should be noted that radical cation 4-chloroanisole, a close analogue of 2,4,5-T is characterized in the literature by the absorption band maximum centred at 475 nm [15]. The absorption observed at the time moment of greater than 8 µs (see Fig. 3, *a*, *b*), to all appearance, corresponds to the formation of 2,4,5-trichlorophenol phenoxyl radical resulting from the attacking on the radical cation by the solvent [15].

Figure 4, *a*, *b* demonstrates kinetic curves for the absorption connected with disappearing the transient species at the wavelengths of 480 and 720 nm under different initial intensity of the excitation pulse. These curves can be approximated well by a biexponential function

$$\Delta A = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \qquad (5)$$

wherein $A_1$, $A_2$, $A_3$ are the absorption amplitude for radical cation, hydrated electron and phenoxyl radical, respectively; $\tau_1$, $\tau_2$ are the observed lifetime values for radical cation and hydrated electron, respectively.

The characteristic lifetime values determined for radical cation and hydrated electron amounted to 130 ns and 1 μs, respectively.

From the ratio between amplitudes $A_1$ (480 nm) and $A_2$ (720 nm) and taking into account the known extinction coefficient for hydrated electron [12] one could estimate the extinction coefficient inherent in the radical cation equal to $\varepsilon^{480} \approx 2 \cdot 10^4 \, M^{-1} \cdot cm^{-1}$.

The main channels of the hydrated electron disappearance in oxygen-free solutions could consist in capturing by 2,4,5-T to form a radical anion, and recombining with the radical cation to regenerate the parent compound. Since the concentration of the radical cation is significantly less than the initial acid concentration, the recombination reaction could be neglected and the rate constant of capturing the hydrated electron by the pesticide should be estimated as $k = (\tau_2[2,4,5\text{-}T])^{-1} \approx 7 \cdot 10^9 \, M^{-1} \cdot cm^{-1})$.

The 2,4,5-T radical cation, to all appearance, undergoes hydrolyzing by a water molecule to form long-lived phenoxyl radical, whose absorption corresponds to the component $A_3$ (see Fig. 4). Basing on the characteristic lifetime of the radical cation (130 ns) and the concentration of solvent, one can estimate the hydrolysis rate constant ($k \approx 1.4 \cdot 10^5 \, M^{-1} \cdot s^{-1}$). It could be assumed that the phenoxyl radical disappears in the reaction with radical anion 2,4,5-T to form final products of 2,4,5-T photolysis. A detailed determination of the mechanism and the rate constants inherent in disappearing the intermediate species is beyond the scope of this paper being the subject of further work.

The yield intermediates depends in a nonlinear manner on the intensity of the excitation pulse (see Figs. 3, *b* and 4), which indicates the fact that there is the contribution of the two-photon ionization observed under a high power laser pulse:

$$2,4,5\text{-}T \xrightarrow{\;2h\nu\;} [ArOAc]^{+\bullet} + e_{aq}^{-} \qquad (6)$$

The approximation of the experimental data at 720 nm concerning the yields of the hydrated electron according to the formula (see Fig. 3, *b*)

$$\Delta A = aI + bI^2 \qquad (7)$$

allows one to estimate the quantum yield for the one-photon photoionization of 2,4,5-T $\phi(266\,nm) = 2.3 \cdot 10^{-3}$. The quantum yield observed for the photoionization is equal to 0.03 at the excitation energy amounting to 0.23 J/cm$^2$ (see Fig. 3, *b*).

**CONCLUSION**

UV laser excitation of 2,4,5-trichlorophenoxyacetic acid in aqueous solution results in a one-photon and two-photon ionization of herbicide to form hydrated electron/radical cation pair. In deoxygenated solutions, hydrated electrons disappear due to the reaction of capturing by the initial compound, whereas the radical cation is hydrolyzed by water to form a long-lived phenoxyl radical. In the presence of β- and γ-CD, there is the formation of inclusion complexes observed, which results in changing the rate of pesticide photodegradation.

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