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A mechanistic study of the photodegradation of herbicide 2,4,5-trichlorophenoxyacetic acid in aqueous solution[†][‡]

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Photodegradation of herbicide 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) in aqueous solution was investigated by stationary (254 nm) and nanosecond laser (266 nm) flash photolysis techniques. It was shown that in the primary photochemical step both photoionization (which generates a hydrated electronradical cation pair) and heterolytic cleavage of a C–Cl bond takes place. The major products of substitution of one of the chlorine atoms in the 2-, 4- or 5-position by a hydroxyl group as well as the products of hydroxylation of the benzene ring in 3- and 6-positions were identified by HPLC and LC-MS methods. The complexation of 2,4,5-T with β - and γ -cyclodextrins ($\beta(\gamma)$ CD) was investigated. The influence of such complexation on the quantum yield of herbicide photolysis and on the ratio of photodegradation products was determined.

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1. Introduction

2,4,5-Trichlorophenoxyacetic acid (2,4,5-T) is one of the most widely used herbicides in agriculture.^{1,2} 2,4,5-T as a 2,4,5-trichlorophenol derivative is a toxic contaminant and its appearance in natural water systems leads to deterioration of drinking water quality.^{1,3,4} Photochemical techniques are widely used for water purification, amongst other (bio)chemical approaches.^{5,6}

Cyclodextrins (CD) are cyclic oligosaccharides composed of $6(\alpha$ -CD), $7(\beta$ -CD) or $8(\gamma$ -CD) residues of α -D-glucopyranose molecules joined in macrocycles by α -D-1,4-glycosidic linkages. Such a structure ensures the presence of an inner hydrophobic cavity and an external hydrophilic periphery which allows them to form "host-guest" inclusion complexes with various hydrophobic molecules. Such complexation often leads to significant changes in the "guest" molecule photochemistry and photophysics, and to an increase of the "guest" photodegradation in particular. Recently, it has been shown that complexation with CD can be used in the development of new catalytic

techniques of photochemical cleaning in solutions and solids. $^{7-9}$

Stationary photolysis of an aqueous solution² and photocatalytic decomposition of 2,4,5-T in presence of titanium dioxide^{6,10} with formation of major photodegradation products (different chlorophenols and products of carboxymethyl group oxidation and hydrolysis) have been described previously. Whilst flash photolysis experiments with 2,4,5-T have not been reported, there is information available on the mechanism of photodecomposition of *p*-chloroanisole – a close analogue of 2,4,5-T. The first stage in the photodecomposition of *p*-chloroanisole is reported to be photoionization with the formation of a hydrated electron–radical cation pair.¹¹ Photoinduced heterolytic cleavage of a C–Cl bond in *p*-chloroanisole has also been reported.¹²

This article describes mechanistic studies of 2,4,5-T photochemistry in aqueous solutions by stationary and laser flash photolysis methods, and also explores the influence of the complexation of 2,4,5-T with β - and γ -cyclodextrins (2,4,5-T- $\beta(\gamma)$ CD) on the photodegradation quantum yield of 2,4,5-T.

2. Materials and methods

2,4,5-Trichlorophenoxyacetic acid (Sigma-Aldrich, >97%), and β - and γ -cyclodextrins (Wako Pure Chemical Inc, >97%) were used without further purification. The experiments were performed in aqueous solutions (pH 9–10) at 2,4,5-T concentration range 10^{-5} – 10^{-3} mol l⁻¹. 2,4,5-T concentrations were

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Fig. 1 Structural formulae of 2,4,5-trichlorophenoxyacetic acid, and β - and γ -cyclodextrins.

calculated using extinction coefficient $\varepsilon = 2340 \text{ M}^{-1} \text{ cm}^{-1}$ ($\lambda = 289 \text{ nm}$). $\beta(\gamma)CD$ concentration range was 10^{-4} – 10^{-2} mol l⁻¹. Chemical structures of 2,4,5-T, and β - and γ -CD are shown in Fig. 1.

UV absorption spectra were recorded using an Agilent 8453 spectrophotometer (Agilent Technologies). A set-up for laser flash photolysis which utilizes the fourth harmonic (266 nm) of a Nd:YAG laser (LS-2137U, Solar, Belarus) as an excitation source (pulse duration 6 ns, pulse energy 1–20 mJ per pulse)¹³ was used in the experiments. The time resolution of the set up was 50 nanoseconds. Steady-state photolysis was also performed using a medium-pressure mercury lamp DRShA-250 with a set of glass filters for selecting the wavelength at 254 nm (mean energy 0.55 mW). For calculation of quantum yields (mean errors \pm 20%), laser and lamp intensity were measured by means of SOLO 2 laser power and energy meter (Gentec EO).

LCMS experiments were performed using ionic trap Esquire 6000 (Bruker Daltonics) with the HPLC-separation system Agilent 1200 Series. Separation was performed on an analytical column Zorbax SB300-C8, 1.0×150 mm, 3.5μ m in gradient acetonitrile (ACN)/0.1% formic acid (FA): 2% (0–5 min), 2–40% (5–10 min), 40–95% (10–37 min), 95% (37–43 min), 95–2% (43–44 min), 2% (44–55 min): flow rate 50 µl min⁻¹, sample volume 8 µl. Experimental parameters: ion scanning in negative mode in the range 50–1000 *m/z*, HV Capillary 4000 V, HV End Plate –500 V, nebulizer pressure 20 psi, desiccative gas flow (N₂) 10 l min⁻¹, temperature 300 °C. Tandem breaking of ions was performed in an automatic mode.

¹H NMR spectra were recorded on a BRUKER DPX200 NMR spectrometer (200 MHz ¹H operating frequency, (τ (90°) = 7.2 µs) at 20 °C.

HPLC experiments were performed using the liquid microcolumn chromatograph Milichrom A-02 with ProntoSIL 120-5-C18 AQ #1810 column, 2.0×75 mm, 5 µm. The eluent was a mixture of acetonitrile with water buffer solution (0.2 M LiClO₄ (Aldrich) and 0.005 M HClO₄ (Aldrich), gradient 10%–100% acetonitrile. Flow rate was 100 µl min⁻¹, sample volume was 15 µl, column thermostat temperature -40 °C. UV-detection was performed at eight wavelengths: 210, 220, 230, 240, 250, 260, 280 and 300 nm.

All photochemical experiments were performed in a 1 cm quartz cell in air- or argon-saturated samples at temperature 298 K under atmospheric pressure.

3. Results and discussion

3.1. Complexation of 2,4,5-T with $\beta(\gamma)$ CD

The addition of cyclodextrins leads to a change of 2,4,5-T optical and NMR spectra. In particular, the resonances due to aromatic protons changing shape and chemical shifts indicates that a complexation process takes place (Fig. 2a, inset):

$$2,4,5-T + CD \leftrightarrow 2,4,5-T-CD \text{ (complex)}$$
 (1)

Fig. 2a shows the change in the observed chemical shifts of 2,4,5-T protons *versus* β -CD concentration obtained in the course of NMR titrations. This dependence is usually used to calculate the stability constant from fitting the curve obtained assuming a particular ratio of host and guest concentrations.¹⁴ For 1:1 complex stoichiometry with similar guest and host



Fig. 2 (a) Nonlinear fit (solid line) of chemical shifts of 2,4,5-T protons with variation of β -CD concentration. Inset: Fragments of the ¹H NMR spectra of 2,4,5-T in free state and in complex with β -CD and γ -CD. (b) Job's plot¹⁵ for [2,4,5-T– β CD] and [2,4,5-T– γ CD] systems.

 $\label{eq:table_$

	$K_{\rm st}$ (M)	ε^{289}	Diameter (Å)
2,4,5-T-αCD	_	—	4.7-5.3
2,4,5-T–βCD	370	2200	6.0 - 6.5
2,4,5-T-γCD	_	2100	7.5-8.3

concentrations, the concentration of the complex obeys the following equation:

$$[2,4,5\text{-}T\text{-}CD] = \frac{1}{2} \times \left(\frac{1}{K_{\text{st}}} + [2,4,5\text{-}T]_0 + [CD]_0\right) \\ -\frac{1}{2} \times \sqrt{\left([2,4,5\text{-}T]_0 + [CD]_0 + \frac{1}{K_{\text{st}}}\right)^2 - 4[2,4,5\text{-}T]_0[CD]_0}$$
(2)

where $[2,4,5\text{-T}]_0$ is the 2,4,5-T concentration, $[\text{CD}]_0$ is the CD concentration, K_{st} is the stability constant. In the presence of β -CD formation of 1:1 inclusion complex was observed (Fig. 2b), whilst the 2,4,5-T inclusion complex with γ -CD had 2:1 stoichiometry (Fig. 2b), which makes the determination of the stability constant for this species difficult.

The calculated values of stability constants (K_{st}) and absorption coefficients of 2,4,5-T and 2,4,5-T–CD complexes are given in Table 1. No complexation with α -CD was observed due to geometrical reasons, as diameter of the internal cavity of α -CD is smaller than the diameter of 2,4,5-T (Table 1, Fig. S1 in ESI‡).

3.2. Laser flash photolysis of 2,4,5-T

Excitation of deoxygenated 2,4,5-T solutions (266 nm) with a laser pulse leads to an appearance of a transient absorption spectrum, composed of two bands with maxima at \approx 500 and 720 nm (Fig. 3a). The transient absorption features at these wavelengths disappear with considerably different rates (Fig. 4), which indicates the presence of two transient species. From pulse radiolysis studies it is known that the broad band with the maximum at 720 nm can be attributed to an absorption of hydrated electron (e_{aq}^{-} , $\varepsilon^{720} = 2.27 \times 10^4$ M⁻¹ cm⁻¹)^{16,17}. Therefore, UV-excitation of 2,4,5-T results in its photoionization accompanied by generation of a hydrated electron–radical cation ([ArOAc]⁺⁻) pair, which is a typical feature of the photochemistry of phenols in aqueous solutions.^{11,18,19}

$$2,4,5\text{-T} \xrightarrow{h\nu} [\text{ArOAc}]^{+\bullet} + e_{aq}^{-}$$
(3)

The second absorption band with maximum at 500 nm can be attributed to a radical cation (Fig. 3a). It is worth noting that the radical cation of *p*-chloroanisole, which is a close analog of 2,4,5-T, exhibits an absorption band with a maximum at 475 nm.¹⁷ Long-lived absorption observed on a time scale longer than 8 μ s (Fig. 3a, b) corresponds probably to the 2,4,5-trichlorophenol phenoxyl radical, which is formed



Fig. 3 (a) Transient absorption spectra registered at 0.05 (1), 0.4 (2), 1.6 (3), 4 (4) and 48 (5) µs after laser excitation of 2,4,5-T (4 × 10⁻⁵ M). Dotted line: Absorption spectrum of hydrated electron taken from.¹⁶ (b) Transient absorption spectra registered at 0.05 (1), 0.4 (2), 1.2 (3), 2.4 (4) and 48 (5) µs after laser excitation of 2,4,5-T (4 × 10⁻⁵ M) with γ -CD (1 × 10⁻² M).

as a result of the reaction between the radical cation and the solvent molecule: 11

$$[ArOAc]^{+} + H_2O \rightarrow ArO + AcOH + H^{+}$$
(4)

Fig. 4a, b demonstrates kinetic traces of the decay of the transient absorption bands at 480 and 720 nm obtained under different excitation energies. Kinetic curves at both wavelengths could be globally fitted by the two-exponential function (5), which allows one to identify typical lifetimes of the radical cation ($\tau_1 = 130$ ns) and hydrated electron ($\tau_2 = 1 \ \mu$ s).

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

One can estimate the radical cation extinction coefficient, which is equal to $\epsilon^{480} \approx 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, by the ratio of amplitudes A_1 (480 nm) and A_2 (720 nm) and known absorption coefficient of the hydrated electron.¹⁶

In deoxygenated solutions the main decay channels of hydrated electrons should be capture by 2,4,5-T and recombination with the radical cation followed by regeneration of the initial compound. Since the concentration of the radical cation



Fig. 4 Kinetic curves at 480 (a) and 720 (b) nm. (1–3) 4.7, 6.5 and 9.7 mJ per pulse, accordingly. Smooth curves: Global fit by formula (5) with $\tau_1 = 130$ ns and $\tau_2 = 1 \ \mu$ s. [2,4,5-T] = 1.7 × 10⁻⁴ M. Inset to b: The dependence of 1/ τ_2 on [2,4,5-T].

is much lower than the initial concentration of 2,4,5-T, the recombination reaction can be neglected and one could estimate the rate constant of capture of the hydrated electron by pesticide ($k_e = (\tau_2[2,4,5\text{-T}])^{-1} \approx 7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) with the formation of 2,4,5-T radical anion (Fig. 4b, inset). The latter species undergo Cl⁻ elimination with formation of the phenyl radical,²⁰ which is not detectable in our flash photolysis experiments due to weak absorbance in the spectral region investigated.²¹

In turn, the radical cation of 2,4,5-T undergoes hydrolysis leading to the generation of a long-lived phenoxyl radical, whose absorption corresponds to a long-lived component A_3 (Fig. 4a, b). Using the radical cation characteristic lifetime (130 ns) and solvent concentration, one can estimate the rate constant of such hydrolysis processes ($k_h \approx 1.4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$). The phenoxyl radical decays probably in a reaction with the phenyl radical, and in various self-reactions leading to the formation of final photolysis products. A detailed definition of mechanism and intermediate decay rate constants in argon-saturated solutions is outside the scope of this article and will be the subject of further studies.



Fig. 5 Dependence of the initial absorption of hydrated electron at 720 nm on the laser pulse energy, calculated with the eqn (7). Smooth curve: Best fit obtained with eqn (7). Experimental data: open circles – 2,4,5-T (4 × 10⁻⁵ M), black stars – 2,4,5-T (4 × 10⁻⁵ M) with γ -CD (1 × 10⁻² M).

The yields of the intermediate species exhibit nonlinear dependence on the excitation energy (Fig. 5). This nonlinearity indicates some contribution from the two-photon ionization which can occur at higher laser pulse intensities (eqn (6)).

2,4,5-T
$$\xrightarrow{2h\nu}$$
 [ArOAc]^{+•} + e_{aq}⁻ (6)

Experimental data on the yield of hydrated electron at 720 nm were approximated by eqn (7) (Fig. 5):

$$\Delta A = a \times I + b \times I^2 \tag{7}$$

which allows one to estimate quantum yield of one-photon ionization of 2,4,5-T, $\phi^{266nm} = 2.3 \times 10^{-3}$. The observed photo-ionization quantum yield equals 0.03 under excitation energy of 0.23 J cm⁻² (Fig. 5).

UV excitation (266 nm) of the deoxygenated solutions of the 2,4,5-T- γ CD inclusion complex leads to results similar to those obtained for the free 2,4,5-T (Fig. 3b). The formation of both the radical cation and of the hydrated electron was observed. It is worth noting that the yield (Fig. 5) and the lifetime of the radical cation (115 ns) and hydrated electron (1.2 μ s) are very similar, within the experimental error, to the corresponding values obtained in the experiments with the free 2,4,5-T.

3.3. Stationary photolysis of 2,4,5-T and its complexes with β CD in aqueous solution

Liquid chromatography of photolyzed solutions of 2,4,5-T indicates that several aromatic products are formed in the process of the photolysis (Fig. 6a,b). Optical absorption spectra of the main photoproducts are given on Fig. 6c. The presence of an absorption band near 290 nm indicates that the benzene ring of 2,4,5-T is not affected by the photolysis. Analysis of the mass-spectroscopic data (Table 2) leads to the conclusion that the are two types of products: (i) the products formed as a result of the substitution of one of the chlorine atoms in either



Fig. 6 (a) HPLC chromatograms of 2,4,5-T with (1) and without (2) β -CD during photolysis at 254 nm in air-equilibrated aqueous solution (UV detector wavelength: 280 nm). [2,4,5-T] = 8 × 10⁻⁴ M, [β -CD] = 5 × 10⁻³ M, pH 9. (b) Evolution of 2,4,5-T and photoproduct absorbance at 280 nm during photolysis. (c) Normalized optical spectra of 2,4,5-T and of the photoproducts.

Table 2	LCMS	results	of	irradiated	2,4,5-T
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Retention time/min	m/z	Proposed structure
13.1	235/237/239 – main ion ^{<i>a</i>} , 199/201 – loss of one chlorine atom, 177/179 – loss of acetic group	Product of substitution of one chlorine atom by a hydroxyl group
13.6	285/287/289 – main ion, 251/253/255 – loss of two hydroxyl groups, 227/ 229/231 – loss of acetic group, 193/195 – loss of one chlorine atom and acetic group	Product of hydroxylation on 3- and 6-position of the benzene ring
14.0	235/237/239 – main ion, 199/201 – loss of one chlorine atom, 177/179 – loss of acetic group	Product of substitution of one chlorine atom by a hydroxyl group
14.5	235/237/239 - main ion, 199/201 - loss of one chlorine atom, 177/179 - loss of acetic group	Product of substitution of one chlorine atom by a hydroxyl group
16.1	253/255/257 – main ion, 195/197 – loss of acetic group	2,4,5-T

^{*a*} Three or two m/z signals indicate distribution of isotopes Cl-35 and Cl-37 in the photodegradation products and in 2,4,5-T.

2-, 4- or 5-position by the hydroxyl group, and (ii) the products of hydroxylation at 3- and 6-positions of the benzene ring. The quantum yield of 2,4,5-T photolysis (ϕ^{254nm}) calculated from the HPLC data (Fig. 6b) is equal to 0.014 and matches well the value of 0.015 (290 nm) published in ref. 22. It is worth noting that ϕ^{254nm} is much higher than the value of the quantum yield of one-photon ionization (ϕ^{266nm}), which indicates that photoionization is not the main photochemical channel of the photodegradation of 2,4,5-T.

The nature of the main photoproducts allows us to conclude that the channel of photodegradation is heterolytic cleavage of a C–Cl bond with the formation of phenyl cation (eqn (8)) followed by a fast nucleophilic attack by a solvent molecule (eqn (9)):^{12,23}



The phenyl cation is not observed in our flash photolysis experiments probably due to its weak absorbance in the near UV region, and the short lifetime outside of our detection range.

The presence of 5×10^{-3} M β -CD (84% of 2,4,5-T- β CD complex) decreases the quantum yield of 2,4,5-T photolysis (to 0.009) and affects the nature of the photodegradation products, which could be clearly demonstrated by HPLC results (Fig. 6a). Formation of the new peaks with retention time in the range 20–23 min was observed with the simultaneous decrease in the intensity of the products with retention times 10.6, 14.6 and 25.1 min. Thus, presence of cyclodextrins in the solution has not accelerated the 2,4,5-T photodegradation. Detailed analysis of 2,4,5-T degradation products in its inclusion complex with β -CD will be the subject of further study.

Conclusions

The UV excitation of herbicide 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) in aqueous solution leads to (i) heterolytic cleavage of a C–Cl bond and formation of the corresponding cation of di-Cl-phenoxyacetic acid, and (ii) ionization of the herbicide which generates a hydrated electron-radical cation pair. In deoxygenated solutions, the hydrated electron is captured by 2,4,5-T, whilst the radical cation undergoes hydrolysis and generates of a long-lived phenoxyl radical. The major photochemical products arise from (i) the substitution of one chlorine atom in either 2-, 4- or 5-position by hydroxyl groups, and (ii) the products of hydroxylation of the benzene ring in 3- and 6-positions.

In the presence of β -CD and γ -CD, formation of inclusion complexes is observed. Such complexation decreases the photodegradation quantum yield of 2,4,5-T and leads to changes in the nature and relative yields of the photodegradation products. Therefore, complexation with cyclodextrins does not promote removal of 2,4,5-T from aqueous solution, and development and application of other techniques is required in order to achieve effective photodegradation of this herbicide.

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Notes and references

- 1 *Encyclopedia of Occupational Health and Safety*, ed. J. M. Stellman, International Labour Organization, 4th edn, 1998, vol. 4, p. 287.
- 2 D. G. Crosby and A. S. Wong, J. Agric. Food Chem., 1973, 21 (6), 1052.
- 3 Y. David and J. H. Lai, J. Environ. Sci. Health, 1984, C2(2), 135.
- 4 Health Criteria and other supporting information, *Guidelines for Drinking-Water Quality*, 2nd edn, World Health Organization, Geneva, 1996, vol. 2, 973.
- 5 M. R. Hoffmann, S. T. Martin, W. Choi and D. W. Bahneman, *Chem. Rev.*, 1995, **95**, 69.
- 6 K. Tanaka and K. S. N. Reddy, Appl. Catal., B, 2002, 39, 305.
- 7 S. Ishiwata and M. Kamiya, Chemosphere, 1999, 39, 1595.
- 8 J. Villaverde, C. Maqueda, T. Undabeytia and E. Morillo, *Chemosphere*, 2007, **69**, 575.
- 9 G. Wang, X. Xue, H. Li, F. Wu and N. Deng, *J. Mol. Catal. A: Chem.*, 2007, **276**, 143.
- M. Barbeni, M. Morello, E. Pramauro, E. Pelizzetti, M. Vincenti, E. Borgarello and N. Serpone, *Chemosphere*, 1987, 16, 1165.

- 11 J. P. Da Silva, S. Jockusch, J. M. G. Martinho, M. F. Ottaviani and N. J. Turro, *Org. Lett.*, 2010, **12**, 3062.
- 12 J. P. Da Silva, S. Jockusch and N. J. Turro, *Photochem. Photobiol. Sci.*, 2009, **8**, 210–216.
- 13 I. P. Pozdnyakov, V. F. Plyusnin, V. P. Grivin, D. Y. Vorobyev, N. M. Bazhin and E. Vauthey, *J. Photochem. Photobiol.*, A, 2006, **181**, 37.
- 14 H.-J. Schneider, F. Hacket, V. Rudiler and H. Ikeda, *Chem. Rev.*, 1998, **98**, 1755.
- 15 K. A. Connors, Building Constants, The Measurement of Molecular Complex Stability, Wiley-Interscience, New-York, 1987, p. 24.
- 16 G. V. Buxton, C. L. Greenstock, W. P. Helman and A. B. Ross, J. Phys. Chem. Ref. Data, 1988, 17, 513–887.
- 17 P. M. Hare, E. A. Price and D. M. Bartels, *J. Phys. Chem. A*, 2008, **112**, 6800.
- 18 C. Richard and G. Grabner, The handbook of environmental chemistry, in *Environmental Photochemistry*, ed.
 P. Boule, Springer-Verlag, Heidelberg, Berlin, 1999, Part L, p. 218.
- 19 T. A. Gadosy, D. Shukla and L. J. Johnston, *J. Phys. Chem. A*, 1999, **103**, 8834.
- 20 R. M. Quint, H. R. Park, P. Krajnik, S. Solar, N. Getoff and K. Sehested, *Radiat. Phys. Chem.*, 1996, 47, 835.
- 21 B. Cercek and M. Kongshaug, J. Phys. Chem., 1970, 74, 4319-4322.
- 22 Y. I. Skurlatov, R. G. Zepp and G. L. Baughman, *J. Agric. Food Chem.*, 1989, **31**, 1085–1071.
- 23 G. Grabner and C. Richard, The handbook of environmental chemistry, in *Environmental Photochemistry*, ed. P. Boule, D. W. Bahnemann and P. K. J. Robertson, Springer-Verlag Heidelberg, Berlin, 2005, vol. 2, Part M, pp. 161–192.