Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2020, **30**, 439–441

Mendeleev Communications

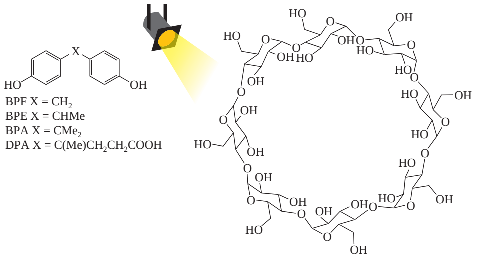
Influence of β-cyclodextrin complexation on photochemistry of bisphenols in aqueous solutions

Victoria A. Salomatova,*[a] Ivan P. Pozdnyakov,[a,b] Peter S. Sherin,[b,c] Dineep Devadasan,[d] Charuvila T. Aravindakumar,[d] Vjacheslav P. Grivin[a,b] and Victor F. Plyusnin[a,b]

[a] *V. V. Voevodsky Institute of Chemical Kinetics and Combustion, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation. E-mail: salomatova@ngs.ru*
[b] *Novosibirsk State University, 630090 Novosibirsk, Russian Federation*
[c] *International Tomography Center, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation*
[d] *Mahatma Gandhi University, 686560 Kottayam, Kerala, India*

DOI: 10.1016/j.mencom.2020.07.011

Influence of complexation with β-cyclodextrin on photochemical properties of four bisphenols has been investigated. Stoichiometry of the inclusion complexes formed has been found to be 1 : 1 and association constants have been calculated from fluorescence experiments. The complexation leads to significant increase in the values of degradation and photoionization quantum yields, which is promising for the development of water decontamination methods.



Keywords: bisphenols, endocrine disruptors, β-cyclodextrin, complexation, photodegradation.

Increasing pollution of Earth's surface and groundwater by organic and inorganic contaminants becomes one of the key environmental problems facing humanity. Bisphenols (BPs) are industrial chemicals widely used in production of epoxy resins, food coating materials, polycarbonate plastic and dental sealants. Extensive manufacture and consumption of BP-based goods leads to release of BPs into environment and food.[1,2] BPs and their derivatives are typically toxic, exhibit endocrine disrupting estrogenic activity[3] and in some cases genotoxicity.[4] Moreover, they are potentially dangerous at very low concentrations[5] and the BP consumption by living organisms can be of high risk for their health and reproductive functions.[6]

Conventional treatment techniques are not effective enough for the removal of BPs from polluted water,[7] this leads to the great interest in a search for alternative purification methods. Various photochemical approaches were demonstrated to be more or less effective for the BPs decomposition, they included direct UV photolysis[8] as well as photolysis in the presence of hydrogen peroxide,[8] titanium dioxide,[9] Fenton reagent,[10] ferric oxalate complex[11] and humic substances.[12]

Cyclodextrins (CDs) represent cyclic oligosaccharides consisting of six (α-CD), seven (β-CD) or eight (γ-CD) α-D-glucopyranoside 1,4-linked units with hydrophilic exterior and hydrophobic internal cavity. Due to such a structure, CDs can efficiently bind a variety of organic molecules by the 'host–guest' inclusion mechanism. This specific property as well as commercial availability accompanied by the absence of toxicity make CDs promising materials for a water decontamination technique alternative to the employment of photocatalysts such as titanium dioxide[13] or forq modification of semiconductor nanoparticles to increase their photocatalytic decoloration activity.[14] It is also possible to produce CD-based insoluble porous polymers[15] for further development of rechargeable photocatalytic materials.

It is known,[16] that β-CD and its derivatives form inclusion complexes with BPs A (BPA), B (BPB), F (BPF) and S (BPS). As well, β-CD was reported to enhance degradation rates of BPA and its analogues.[17–21] These data are based on the pseudo-first-order kinetic model, though it seems more practical to deal with quantum yield (QY) values, because they depend much less on experimental conditions. In this work, we investigated the influence of β-CD on photochemical properties of four BPs in aqueous solutions, namely BPA or 4,4′-(propane-2,2-diyl)bisphenol, BPE or 4,4′-ethylidenebisphenol, BPF or 4,4′-methylenebisphenol and 4,4-di(4-hydroxyphenyl)pentanoic acid (diphenolic acid, DPA), with a special focus on the determination of quantitative photochemical parameters including QYs.[†]

Addition of β-CD to BP solutions had small influence on the intensities and positions of maxima for their long-wavelength absorption bands [Figure 1(*a*)]. The fluorescence maxima were

---

[†] BPs A, E, F and DPA (Damao Chemicals Co., China, > 99.0% purity) as well as β-CD (Wako Pure Chemical, China, > 97% purity) were used without further purification and dissolved in double-distilled water. All the photochemical experiments were performed in a 1 cm quartz cell in air-equilibrated solutions using a XeBr excimer lamp with excitation wavelength of 282 nm for steady-state irradiation as well as a laser flash photolysis setup with an LS-2137U Nd:YAG laser (Lotis TII, Belarus) with excitation wavelength of 266 nm, pulse duration 5–6 ns, illumination spot area 0.03 cm^2 and energy per pulse up to 10 mJ for time-resolved experiments, the device was similar to that described.[21] The lamp and laser intensities were measured using a SOLO 2 laser power meter (Gentec-EO, Canada). UV spectra were recorded on an Agilent 8453 spectrophotometer. Fluorescence spectra were recorded using an FLS-920 spectrofluorimeter (Edinburgh Instruments). Ozone-free xenon lamp Xe900 (λ_{ex} = 260 and 280 nm) was used as an excitation source. The irradiated samples were quantified with an HPLC Agilent LC 1100 system (USA) equipped with a diode array detector. HPLC separations were performed using a Zorbax Eclipse XBD-C18 Rapid Resolution column (4.6 × 100 mm, 80 Å, 1.8 μm) with a flow rate

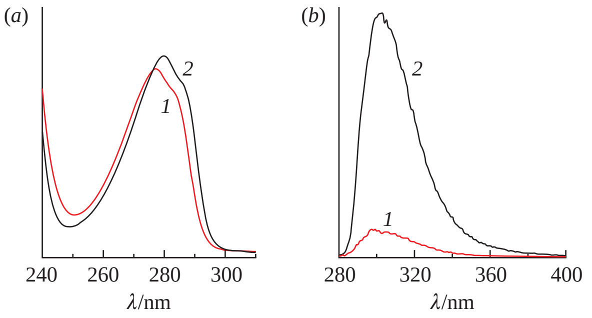


Figure 1 (*a*) UV spectrum of BPA (*1*) before and (*2*) after addition of β-CD as well as (*b*) fluorescence spectrum of BPA (*1*) before and (*2*) after addition of β-CD. [BPA] = [β-CD] = 1×10^{-5} mol dm^{-3}.

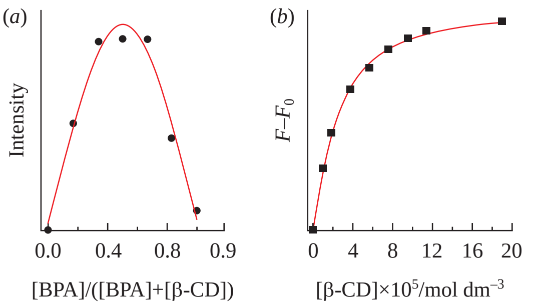


Figure 2 (*a*) Job's plot for BPA–β-CD solutions at total [BPA]+[β-CD] in each point equal to 1 × 10^{-4} mol dm^{-3} as well as (*b*) (F–F_0) value *vs.* [β-CD] fitted by equation (1) at [BPA] = 1 × 10^{-5} mol dm^{-3} and [β-CD] from 0 to 2 × 10^{-4} mol dm^{-3}.

also insensitive to β-CD, however the fluorescence intensities [Figure 1(*b*)] and lifetimes (not shown) substantially increased upon complexation with β-CD for all the explored BPs. This phenomenon was found for DPA in our work,[22] and it had been established that the observed effect of the excited state lifetime prolongation originated from its protection from quenching by the solvent molecules during the BP entry into the CD cavity. The stoichiometry of the complexes was established by the Job's method.[23] Figure 2(*a*) demonstrates the characteristic bell-shaped Job's plot obtained for BPA, where the curve maxima at a point with 0.5 molar fraction of BPA indicates the 1 : 1 stoichiometry of BPA–β-CD complex. The association constant K_{assoc} of BP–β-CD complex can be calculated from the dependence of integral fluorescence changes *vs.* β-CD concentration using equation (1), which represents a common solution for the complexation in the ratio 1 : 1 [Figure 2(*b*)]:

$$F - F_0 = \frac{(\beta - \alpha)}{2}\left[\left([\mathrm{BP}]_0 + [\mathrm{CD}]_0 + \frac{1}{K_{\text{assoc}}}\right) - \right.$$
$$\left. - \sqrt{\left([\mathrm{BP}]_0 + [\mathrm{CD}]_0 + \frac{1}{K_{\text{assoc}}}\right)^2 - 4[\mathrm{BP}]_0[\mathrm{CD}]_0}\,\right], \qquad (1)$$

where F is integral fluorescence intensity of the complex solution; F_0 is integral fluorescence intensity of initial BP solution without β-CD; $[\mathrm{BP}]_0$ and $[\mathrm{CD}]_0$ are initial concentrations of BP and β-CD, respectively; coefficients $\alpha = 2.3 \times \varphi_{\mathrm{BP}} \times \varphi_{\mathrm{BP}}$ and $\beta = 2.3 \times \varphi_{\mathrm{BP-CD}} \times \varepsilon_{\mathrm{BP-CD}}$ are calculated using φ_{BP}, $\varepsilon_{\mathrm{BP}}$ and $\varphi_{\mathrm{BP-CD}}$, $\varepsilon_{\mathrm{BP-CD}}$, which represent QYs and molar absorption coefficients for BP and BP–β-CD, respectively.

The results obtained (Table 1) exceed their corresponding known values,[17–19] which can be explained as follows. The Benesi–Hildebrand equation typically used for the determination of association constants has the necessary requirement $[\mathrm{CD}]_0 >> [\mathrm{BP}]_0$ or $[\mathrm{BP}]_0 >> [\mathrm{CD}]_0$, which has not always been met in the referenced works. For the latter results, the fitting using equation (1) should give more correct values.

The QYs of BP photodegradation at λ_{ex} = 282 nm were calculated from HPLC data and collected as well in Table 1. Complexation with β-CD leads to the increase in the photodegradation QY for all the BPs studied, namely *ca.* three times for BPF, *ca.* five times for BPE, *ca.* 10 times for DPA and 12 times for BPA. In our works,[22,24,25] photoionization with generation of the phenoxyl radical–hydrated electron pair was shown to represent the main primary process both for BPs and their complexes with β-CD. Here, QYs of BP photoionization were determined by laser flash photolysis using the known value of absorption coefficient for hydrated electron e^-_{aq} at 720 nm equal to 22700 dm^3 mol^{-1} cm^{-1}.[26] Complexation with β-CD elevates the photoionization QY value for all the BPs investigated (see Table 1), which represents the direct consequence of the prolongation of their excited state lifetime. This also explains an increase in the photodegradation QY with addition of β-CD.

It is known,[9] that direct UV photolysis can be more feasible for the BPA removal compared with the TiO$_2$ photocatalysis, because the latter approach results in generation of genotoxic 3,4-quinone of BPA. For the direct photolysis we observed formation of hydroxylated BPA species with less toxicity than the starting compound. The formation of predominant product with aromatic ring hydroxylation was confirmed by mass spectrometry for all the BPs investigated as well as their complexes with β-CD (Table 2).

However, direct photolysis of BPs has the following disadvantages: (i) low QY of photodegradation (2 × 10^{-3} to 5.4 × 10^{-3} for the BPs explored), which increases after β-CD complexation, with the most significant effect of more than one order of magnitude being observed for BPA, as well as (ii) emerging hydroxylated BPs are more stable than the initial compounds. The dynamics of degradation for BPE and its predominant accumulation/degradation hydroxylated product are demonstrated in Figure 3. It may be assumed that the addition of β-CD accelerates consumption of hydroxylated products along with

Table 1 QYs of photodegradation at λ_{ex} = 282 nm and photoionization at λ_{ex} = 266 nm for BPs and their complexes with β-CD as well as association constants for BP–β-CD complexes.

Compound	Photodegradation QY for BP	Photodegradation QY for BP–β-CD	Photoionization QY for BP	Photoionization QY for BP–β-CD	Formation constant for BP–β-CD K_{assoc}/dm^3 mol^{-1}	Known value of formation constant for BP–β-CD K_{assoc}/dm^3 mol^{-1}
BPF	2.0 × 10^{-3}	6.0 × 10^{-3}	2 × 10^{-2} (ref. 24)	9.6 × 10^{-2}	9.6 × 10^3	6.33 × 10^3 (ref. 17)
BPE	1.7 × 10^{-3}	8.4 × 10^{-3}	8 × 10^{-3}	3.8 × 10^{-2}	4.5 × 10^4	7.81 × 10^3 (ref. 18)
DPA	3.5 × 10^{-3}	3.6 × 10^{-2}	1 × 10^{-2} (ref. 22)	4.1 × 10^{-2} (ref. 22)	4.0 × 10^4	n.d.[a]
BPA	5.4 × 10^{-3}	6.5 × 10^{-2}	2 × 10^{-2}	n.d.[a]	2.0 × 10^5	1.80 × 10^4 (ref. 19)

[a] Not determined.

---

of 0.5 ml min^{-1} employing the mobile phase consisted of a mixture of 0.1% v/v formic acid solutions in (A) water and (B) acetonitrile in the following ratios *vs.* time: 0% B at 0–3 min, 0–80% B at 3–30 min, 80–100% B at 30–31 min, 100% B at 31–37 min, 100–0% B at 37–38 min and 0% B at 38–45 min. The injection volume was 50–100 µl. Photodegradation products were analyzed using an Ultra HPLC UltiMate 3000 RS system (Dionex, Germany) with a maXis 4G high-resolution ESI TOF mass spectrometer (Bruker, Germany).

Table 2 Ion masses of BPs and their predominant photoproducts.

Compound	*m*/*z* of initial BP	*m*/*z* of predominant photoproduct
BPF	199.0768	215.0715
BPE	213.0926	229.0874
DPA	285.0982	303.1075
BPA	227.0936	243.089

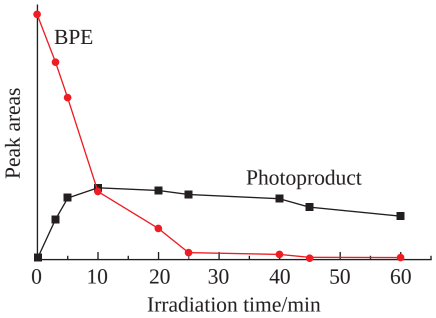


Figure 3 Evolution of MS peak areas for BPE and its predominant photoproduct during irradiation using a XeBr lamp.

initial compounds, though this matter is out of the scope of the present work and is planned to be an object of further investigation.

This work was supported by the Russian Science Foundation (grant no. 18-03-00246). Authors acknowledge the Ministry of Science and Higher Education of the Russian Federation for an access to the mass spectrometry equipment.

References

1 A. V. Krishnan, P. Stathis, S. F. Permuth, L. Tokes and D. Feldman, *Endocrinology*, 1993, **132**, 2279.
2 H. Fromme, T. Küchler, T. Otto, K. Pilz, J. Müller and A. Wenzel, *Water Res.*, 2002, **36**, 1429.
3 T. Suzuki, Y. Nakagawa, I. Takano, K. Yaguchi and K. Yasuda, *Environ. Sci. Technol.*, 2004, **38**, 2389.
4 S. Suarez, R. A. Sueiro and J. Garrido, *Mutat. Res., Genet. Toxicol. Environ. Mutagen.*, 2000, **470**, 221.
5 F. S. vom Saal and C. Hughes, *Environ. Health Perspect.*, 2005, **113**, 926.
6 A. Ullah, M. Pirzada, S. Jahan, H. Ullah, G. Shaheen, H. Rehman, M. F. Siddiqui and M. A. Butt, *Chemosphere*, 2018, **209**, 508.
7 M. Fürhacker, S. Scharf and H. Weber, *Chemosphere*, 2000, **41**, 751.
8 E. J. Rosenfeldt and K. G. Linden, *Environ. Sci. Technol.*, 2004, **38**, 5476.
9 A. O. Kondrakov, A. N. Ignatev, F. H. Frimmel, S. Bräse, H. Horn and A. I. Revelsky, *Appl. Catal., B*, 2014, **160–161**, 106.
10 H. Katsumata, S. Kawabe, S. Kaneco, T. Suzuki and K. Ohta, *J. Photochem. Photobiol., A*, 2004, **162**, 297.
11 D. Zhou, F. Wu, N. Deng and W. Xiang, *Water Res.*, 2004, **38**, 4107.
12 M. Zhan, X. Yang, Q. Xian and L. Kong, *Chemosphere*, 2006, **63**, 378.
13 J. Charles, C. Bradu, N. Morin-Crini, B. Sancey, P. Winterton, G. Torri, P.-M. Badot and G. Crini, *J. Saudi Chem. Soc.*, 2016, **20**, 185.
14 P. Velusamy, S. Pitchaimuthu, S. Rajalakshmi and N. Kannan, *J. Adv. Res.*, 2014, **5**, 19.
15 A. Alsbaiee, B. J. Smith, L. Xiao, Y. Ling, D. E. Helbling and W. R. Dichtel, *Nature*, 2016, **529**, 190.
16 H. Kitano, H. Endo, M. Gemmei-Ide and M. Kyogoku, *J. Inclusion Phenom. Macrocyclic Chem.*, 2003, **47**, 83.
17 J. Xiao, G. Wang, X. Xue, F. Wu, H. Luan and N. Deng, *Environ. Eng. Sci.*, 2007, **24**, 812.
18 G. Wang, X. Xue, H. Li, F. Wu and N. Deng, *J. Mol. Catal. A: Chem.*, 2007, **276**, 143.
19 G. Wang, F. Wu, X. Zhang, M. Luo and N. Deng, *J. Chem. Technol. Biotechnol.*, 2006, **81**, 805.
20 Y. Zhou, X. Gu, R. Zhang and J. Lu, *Ind. Eng. Chem. Res.*, 2015, **54**, 426.
21 I. P. Pozdnyakov, V. F. Plyusnin, V. P. Grivin, D. Yu. Vorobyev, N. M. Bazhin and E. Vauthey, *J. Photochem. Photobiol., A*, 2006, **181**, 37.
22 V. A. Salomatova, I. P. Pozdnyakov, V. V. Yanshole, F. Wu, V. P. Grivin, N. M. Bazhin and V. F. Plyusnin, *J. Photochem. Photobiol., A*, 2014, **274**, 27.
23 P. Job, *Ann. Chim.*, 1928, **9**, 113.
24 V. Salomatova, I. Pozdnyakov, P. Sherin, V. Grivin and V. Plyusnin, *J. Photochem. Photobiol., A*, 2015, **305**, 45.
25 I. P. Pozdnyakov, L. Guo, E. M. Glebov, F. Wu, V. F. Plyusnin, V. P. Grivin and N. Deng, *High Energy Chem.*, 2011, **45**, 214 (*Khim. Vys. Energ.*, 2011, **45**, 245).
26 P. M. Hare, E. A. Price and D. M. Bartels, *J. Phys. Chem. A*, 2008, **112**, 6800.

Received: 9th December 2019; Com. 19/6084