



Photochemistry of chlorobenzene in ice[†]

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Abstract

An unusual photobehaviour of chlorobenzene in ice is reported. Its photolysis at >254 nm provided very different photoproducts from those observed in liquid water where phenol derivatives are almost exclusively isolated. Thus, biphenyl and terphenyl as well as their chlorinated isomers were formed in ice, possibly via a free-radical mechanism, thanks to aggregation of the starting molecules even in very dilute solid solutions. In addition, an unusual multi-step triphenylene photoproduction is reported. Environmental aspects are also discussed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: chlorobenzene; photochemistry; ice; photodegradation; effective reaction cavity; environmental; aggregation.

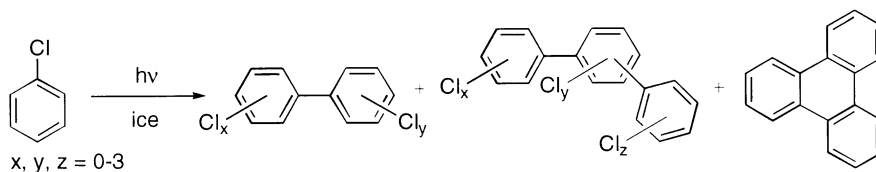
Photochemically induced homolysis of the carbon–halogen bond in haloarenes has been known since the 1960s.¹ Among the aryl halides, chlorobenzene is the best-studied chloroaromatic compound. Photoreductive dechlorination and aryl free-radical coupling reactions were observed in all H-donating non-polar solvents,² in the gas phase,³ and in the solid state.⁴ On the other hand, photosubstitution is the major pathway in methanol⁵ or water/acetonitrile mixtures.⁶ Thanks to its low solubility ($\sim 510 \text{ mg l}^{-1}$ at 25°C⁷), comparatively few reports dealt with studies in water, usually with the emphasis on its environmental fate and photodegradation.⁸ Park and his coworkers have analyzed all the photoproducts from photolysis of chlorobenzene in water.^{8b} In addition to phenol and chloride ion, small amounts of all three phenylphenol isomers were detected (several orders of magnitude lower yield than that of phenol).

Here we present an original investigation of the photobehaviour of chlorobenzene in the solid matrix of ice. Such a medium presents surroundings which might prevent drastic conformational, translational, and rotational changes along the reaction coordinate.⁹ This research is a part of our programme on photochemistry in solid media.¹⁰

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[†] Dedicated to Dr. Alfred Bader for his ‘Chemist Helping Chemists’ activities.

Photolysis of chlorobenzene in ice¹¹ (Scheme 1) was found to be entirely different from that observed in liquid water⁸ where phenol derivatives—products of the radical nucleophilic substitution reaction with the solvent—were almost exclusively isolated. Table 1 lists 22 photoproducts detected after the irradiation of chlorobenzene samples at various concentrations.



Scheme 1.

Table 1
Ice photochemistry of chlorobenzene at -20°C

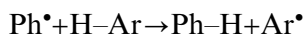
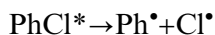
Photoproduct	Retention time ¹¹	$c = 157 \text{ mg l}^{-1}$ a,b	$c = 27 \text{ mg l}^{-1}$ a,c	$c = 4 \text{ mg l}^{-1}$ a,d
Benzene	3.919	1.04	0.50	0.10
Phenol	–	ND	ND	ND
<i>o</i> -, <i>m</i> -, <i>p</i> -Phenylphenol	–	ND	ND	ND
Biphenyl	6.054	1.64	0.26	0.14
<i>o</i> -Chlorobiphenyl	6.349	0.14	0.01	ND
<i>m</i> -Chlorobiphenyl	6.464	1.59	0.11	<0.01 ^f
<i>p</i> -Chlorobiphenyl	7.060	2.22	0.18	–
<i>o</i> -Terphenyl	17.097	0.08	0.01	<0.01
<i>m</i> -Terphenyl	18.525	0.12	0.02	<0.01
<i>p</i> -Terphenyl	19.456	0.12	0.02	<0.01
Chloroterphenyl ^e	17.320–23.379	0.76	0.10	ND
Triphenylene	23.525	0.12	0.01	ND

^a Irradiation of chlorobenzene (with the initial concentration c) at $>254 \text{ nm}$ for 5 hours. The reproducibility was $\pm 10\%$. Product concentrations are in mg l^{-1} . The meaning of ‘ND’ is ‘under the detection limit’. The reaction conversions: ^b $\sim 10\%$, ^c $\sim 30\%$, and ^d $\sim 90\%$, respectively. ^e 13 different isomers found. ^f The total amount of the *m*- and *p*-isomers.

The results suggest that the coupled photoproducts were formed in ice thanks to intermolecular reactions of the starting molecules, which, remarkably, showed no reactivity towards the water molecules of the solvent cavity walls (neither phenol or phenylphenol were detected). Since no diffusion of the chlorobenzene molecules in ice is anticipated, such reactions were caused by the aggregation of molecules in the frozen solvent before and/or during the process of ice solidification. In experiments with a lower chlorobenzene concentration ($\sim 4 \text{ mg l}^{-1}$), many of the photoproducts were still detectable, which means that aggregation still played an important role. The 10–15% loss in the mass balance observed during the experiments suggests the formation of higher-mass compounds that were also detected by the GC analysis.

On the other hand, irradiation of an approx. 0.1% (w/w) mixture of chlorobenzene in ice for 24 hours produced a much more complicated photoproduct mixture, consisting of more than 50 different compounds, including dichlorobenzene, dichlorobiphenyl, and dichloroterphenyl isomers.^{10b} Such observations parallel the study of the photochemistry of *neat* chlorobenzene in that the formation of various polychlorinated biphenyls was reported.⁴

We assume that bond homolysis and reactions of the free radicals so formed take part in most of the transformations in ice. The cleavage of the aryl carbon–halogen bond affords aryl free radicals that can either arylate a suitable aromatic reaction partner or abstract hydrogen from a H-donor:



The quantum efficiencies for the reactions in ice (Table 2) were estimated by photolyzing separately chlorobenzene samples in ice and in methanol, in which the quantum yield of the anisole production at -20°C is known.^{5a} The quantum efficiencies were correlated with the optical densities of the *liquid* solutions. The values in the solid solutions are expected to be smaller due to light scattering, reflection, and a different absorption by the solid material.^{10a}

Table 2
Quantum efficiencies of the photoproduct formation at -20°C ^a

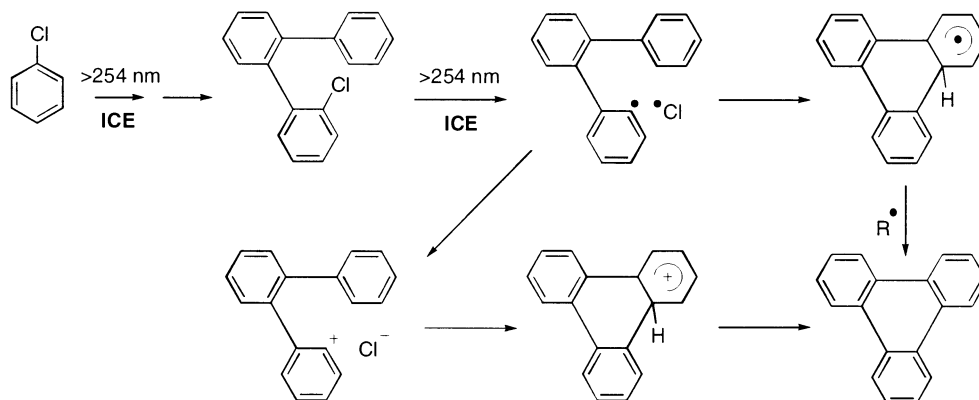
Photoproduct	$c = 157 \text{ mg l}^{-1}$ ^b	$c = 27 \text{ mg l}^{-1}$ ^b
Biphenyl	2.01×10^{-3}	5.59×10^{-3}
<i>o</i> -Chlorobiphenyl	0.14×10^{-3}	0.18×10^{-3}
<i>m</i> -Chlorobiphenyl	1.60×10^{-3}	1.94×10^{-3}
<i>p</i> -Chlorobiphenyl	2.23×10^{-3}	3.17×10^{-3}
<i>o</i> -Terphenyl	0.07×10^{-3}	0.14×10^{-3}
<i>m</i> -Terphenyl	0.10×10^{-3}	0.29×10^{-3}
<i>p</i> -Terphenyl	0.10×10^{-3}	0.29×10^{-3}
Triphenylene	0.10×10^{-3}	0.14×10^{-3}

^a The reaction conversion was kept below 15% to avoid the photoproduct interference. Chlorobenzene in methanol was used as an actinometer ($\Phi = 0.022$ for anisole formation at -20°C).^{5a}

^b Initial chlorobenzene concentration c .

The quantum efficiencies of the chlorobiphenyl and terphenyl photoproduct formation were found to be comparable at both chlorobenzene concentrations. However, a regular increase in biphenyl efficiency with decreasing concentration suggests that dimerisation becomes the most probable reaction due to the smaller number of the starting molecules in the aggregates.

The concentration independent regioselectivity of chlorobiphenyl and terphenyl formation (*m*- and *p*-isomers are strongly preferred) indicates the presence of steric rather than electronic effects in the aggregation. The production of triphenylene in relatively large amounts is quite intriguing. We propose a mechanism, in which photochemically formed 2''-chloro-[1,1';2',1'']-terphenyl cyclises to give triphenylene by either a radical or ionic process as was observed in some other systems¹² (Scheme 2).



Scheme 2.

In conclusion, chlorobenzene does not undergo any photosubstitution reactions with water molecules in ice: the walls of the ice cavity are, in terms of the *effective reaction cavity*,⁹ entirely *hard*. Production of chlorinated biphenyls and terphenyls is, moreover, an environmentally interesting topic. Such reactions can be a *secondary* source of pollution in the polar regions as well as in tropospheric ice cloud particles.

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References

1. Bunce, N. J. In *Organic Photochemistry and Photobiology*; Horspool, W. M.; Song, P.-S., Eds.; CRC: Boca Raton, FL, 1994; pp. 1181–1192 and references therein.
2. (a) Arnold, D. R.; Wong, P. C. *J. Am. Chem. Soc.* **1977**, *99*, 3361–3366. (b) Bunce, N. J.; Bergsma, J. P.; Bergsma, M. D.; De Graaf, W.; Kumar, Y.; Ravanal, L. *J. Org. Chem.* **1980**, *45*, 3708–3713. (c) Bunce, N. J.; Gallacher, J. C. *J. Org. Chem.* **1982**, *47*, 1955–1958.
3. (a) Ichimura, T.; Mori, Y. *J. Chem. Phys.* **1972**, *58*, 288–292. (b) Bunce, N. J.; Landers, J. P.; Langshaw, J.-A.; Nakai, J. S. *Environ. Sci. Technol.* **1989**, *23*, 213–223.
4. (a) Uyeta, M.; Taue, S.; Chikasawa, K.; Mazaki, M. *Nature* **1976**, *264*, 583–584. (b) Georgiou, S.; Koubenakis, A.; Labrakis, J.; Lassithiotaki, M. *J. Chem. Phys.* **1998**, *109*, 8591–8600.
5. (a) Nagaoka, S.; Takemura, T.; Baba, H. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2082–2087. (b) Soumillion, J. P.; DeWolf, B. *J. Chem. Soc., Chem. Commun.* **1981**, 436–437.
6. (a) Choudhry, G. G.; van den Broecke, J. A.; Webster, G. R. B.; Hutzinger, O. *Environ. Toxicol. Chem.* **1986**, *5*, 625–635. (b) Dulin, D.; Drossman, H.; Mill, T. *Environ. Sci. Technol.* **1986**, *20*, 72–77.
7. Gadelle, F.; Koros, W. J.; Schechter, R. S. *J. Colloid Interface Sci.* **1995**, *170*, 57–64.
8. (a) Choudhry, G. G.; Webster, G. R. B.; Hutzinger, O. *Toxicol. Environ. Chem.* **1986**, *13*, 27–83 and references therein. (b) Park, H.-R.; Yang, I.-J.; Kim, M.-S. *Bull. Korean Chem. Soc.* **1998**, *19*, 1265–1268. (c) Tissot, A.; Boule, P.; Lemaire, J. *Chemosphere* **1983**, *12*, 859–872. (d) Boule, P.; Tissot, A.; Lemaire, J. *Chemosphere* **1985**, *14*, 1789–1793. (e) Tissot, A.; Boule, P.; Lemaire, J. *Chemosphere* **1984**, *13*, 381–389. (f) Dullin, D.; Drossman, H.; Mill, T. *Environ. Sci. Technol.* **1986**, *20*, 72–77. (g) Juang, L.-Ch.; Tseng, D.-H.; Lee, J.-F. *Chemosphere* **1998**, *36*, 1187–1199 and references therein.
9. Weiss, R. G.; Ramamurthy, V.; Hammond, G. S. *Acc. Chem. Res.* **1993**, *26*, 530–536.

10. (a) Klán, P.; Janosek, J.; Kriz, Z. *J. Photochem. Photobiol. A, Chem.* **2000**, *134*, 37–44. (b) Klán, P.; Del Favero, D.; Ansorgová, A.; Holoubek, I. *Proc. EUROTRAC Symp.*, in press.
11. Aqueous chlorobenzene solutions (1.4×10^{-3} to 4×10^{-5} M) were prepared by centrifugation of the saturated solution ($\sim 3 \times 10^{-3}$ M) for 5 min at 4°C, followed by dilution. Oxygen was removed from the samples either by bubbling the solutions with argon for 5 min or by sonication. The samples were sealed in quartz tubes (>254 nm irradiation), placed into the merry-go-round apparatus, and irradiated using a 125 W medium-pressure mercury lamp in a cryostat box with ethanol as a cooling medium at –20°C. Solutions were extracted with a dichloromethane solution of hexadecane (2 ml), used as an internal standard. Identification of photoproducts was carried out by GC/MS analysis. The analyses were carried out on a HP 6890 gas chromatograph equipped with an HP 5972 mass selective detector (Hewlett–Packard, USA). A 1 µl sample was introduced in a split mode (20:1 split ratio) into the capillary column DB5-MS (J&W Scientific, Folsom, USA) of 60 m length, 0.25 mm i.d., and 0.25 µm film thickness. The mass spectrometer was operated in the scan mode using EI ionisation; the mass spectra were collected in the mass range 50–550 *m/z*.
12. Grimshaw, J.; de Silva, A. P. *Chem. Rev.* **1981**, *10*, 181–203.