

RADICAL CATIONS OF POLYCHLORINATED AND POLYBROMINATED BIPHENYLS
IN 1,2-DICHLOROETHANE: A PULSE RADIOLYSIS STUDY

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ABSTRACT:

Radical cations from polychlorinated and polybrominated biphenyls in 1,2-dichloroethane have been investigated and their optical and kinetic properties are compared with corresponding data for the biphenyl cation itself. The radical cations exhibit specific absorption spectra with one or two bands in the u.v., and one weak transition in the near i.r. region.

INTRODUCTION:

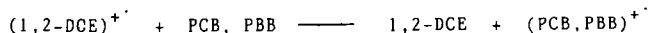
The radical cation of biphenyl in solution exhibits two absorption bands, one with a maximum around 380 nm and the other in the near i.r. at ca. 690 nm^{1,2}. In order to study the influence of the halogen atom and the substitution sites on the positions of the absorption bands and the kinetic characteristics of halogenated radical cations, we have conducted a pulse radiolysis investigation of mono- and polyhalogenated biphenyls^{3,4}.

EXPERIMENTAL PART:

The compounds were commercially available or synthesized as described in the literature. The pulse radiolysis set up and procedures for optical detection and data analysis have been described in the literature⁵. The solutions were generally exposed to short pulses of high-energy electrons (3.8 MeV). Due to the low solubility of the compounds in water solutions were prepared in freshly distilled 1,2-dichloroethane which is an ideal solvent for radiation chemical studies⁶.

RESULTS AND DISCUSSION:

Upon pulse radiolysis of PCBs and PBBs in 1,2-dichloroethane solution, radical cations are produced which display transient absorptions in the u.v. region (one or two bands, 370-420 nm) and in the near i.r. region (usually one weaker band). The radical cation formation via the general reaction:



and their identification has been elaborated in detail in our previous publications^{3,7}.

The absorption bands in the near i.r. are red shifted relative to the corresponding absorption band of the biphenyl cation itself. Substitution in ortho position leads to a blue shift while meta-substitution exerts only a weak effect on the absorptions in the u.v. The life-times of both meta- and ortho-substituted biphenyl radical cations are decreased relative to that of the unsubstituted biphenyl species. Radical cations of ortho-substituted PCBs or PBBs, as well as those containing many vicinal halogen atoms, decay by approximately first-order kinetics. The underlying reaction is assumed to be deprotonation. Radical cations of biphenyls with para-substituents show a red shift in the u.v. absorption and an increase in life-time relative to the corresponding properties of the unsubstituted biphenyl species. Their decay occurs mostly by second-order kinetics. On the basis of these physico-chemical characteristics a probable structure is suggested for the radical cations of halogenated biphenyls.

The distinct optical absorptions in the u.v. and i.r. of the investigated radical cations are indicative of planarization of the radical cations relative to their parent compounds. This possibly corroborates the observed dependence of planarity and toxicity of the PCBs and PBBs⁸.

The maxima of the transient near i.r. absorption bands of the monohalogenated biphenyls can be linearly correlated to ionization potentials from photoelectron spectroscopy^{3,9,10}. The data suggest that the investigated monohalogenated and polyhalogenated biphenyls undergo at least partial planarization upon radical cation formation.

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