THERMODYNAMIC PREDICTION OF THE COMPOSITION OF POLYCHLORINATED BIPHENYL NITRATION PRODUCTS AS A FUNCTION OF THE NITRATING MIXTURE EXCESS

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Polychlorinated biphenyls (PCBs) are persistent organic pollutants. The development of effective approaches for their neutralization through a sequence of chemical modification and thermolysis methods is a relevant task. The aim of this study is to perform thermodynamic modeling of electrophilic substitution reactions in a series of PCBs, using the nitration processes of tri- and tetrachlorobiphenyls as an example.

The nitration process was modeled by the HSC software package (0.001 mol PCB, 0.005–0.11 mol HNO_3:H_2SO_4 (1:1), T = 100–200°C). It was found that with a small excess of the nitrating mixture (0.005 mol), the conversion of the initial PCBs is incomplete, with the residual concentration of the parent congener being higher for trichlorobiphenyl than for tetrachlorobiphenyl. Increasing the amount of nitrating mixture to 0.11 mol leads to the complete absence of the initial PCBs in the products, which are represented exclusively by deep nitration products – penta-, hexa-, and heptanitro derivatives.

However, experimental data indicate that as the number of chlorine atoms in the biphenyl structure increases, the proportion of deep nitration products decreases. For 2,4,5-trichlorobiphenyl, a mixture of di- (78%) and trinitro derivatives (22%) was obtained, while for 2,5,3',4'-tetrachlorobiphenyl, a mixture of mono- (15%) and dinitro derivatives (85%) was obtained, contradicting the thermodynamic calculations. This discrepancy is explained by kinetic limitations: thermodynamically permitted reactions may proceed at a slow rate. It is likely that increasing the reaction time would bring the experimental results closer to the thermodynamic equilibrium, and for tetrachlorobiphenyl, the proportion of deeper nitration products would increase, becoming comparable to that for trichlorobiphenyl.

Thus, the modeling confirms the principal feasibility of exhaustive PCB nitration with an excess of the nitrating mixture, taking into account the kinetic factors of the chemical process. The obtained thermochemical data can be used to predict the behavior of other PCB congeners in electrophilic substitution reactions.

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