

PYROLYSIS AND COMBUSTION OF CHLORORSANICS IN DIELECTRIC FLUIDS

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Numerous laboratory simulations and several real world incidents have demonstrated that, under certain conditions, heating of concentrated solutions of polychlorinated biphenyls (PCBs), or tri- and tetrachlorobenzenes (TCBs) can produce significant concentrations of polychlorinated dibenzodioxins (PCDDs) and/or polychlorinated dibenzofurans (PCDFs). However, at the outset of this EPRI-supported project, little was known about the thermal behavior of these compounds when diluted to the 5000-50 ppm concentration range with various retrofill fluids or askarel substitutes. This laboratory has selected two heating regimens for study with the goal of choosing conditions that were distinct from each other as well as those used by earlier and contemporary investigators and that might bear some similarity to potential real world events. At the outset, however, it was recognized that no feasible sequence of laboratory experiments could effectively model the range of possible real world incidents. One set of experiments ("Pyrolysis") involved heating 100 mg solutions of the mixture of interest in long vertically mounted pyrex tubes sealed at one end. The sealed end containing the sample was inserted for 15 minutes into a snugly fitting thermostatically controlled metal block, maintained at constant temperature in the range of 500°C - 650°C. Typically under these conditions, the solution refluxed vigorously about half-way up the tube; additional precautions were taken to assure that all materials were retained in the tube. The initial experimental design called for pyrolysis of neat Aroclor 1254 and 5000 ppm solutions of Aroclor 1254 in mineral oil, silicone oil, and tetrachloroethylene at a range of temperatures sufficient to establish the optimum for PCDF formation. Then, 5000, 500, and 50 ppm solutions of Aroclor 1254 in the three fluids were pyrolyzed at the optimal conditions. Similarly, 1,2,4-trichlorobenzene, 1,2,3,4-tetrachlorobenzene and the 2:1 mixture were pyrolyzed neat and as 5000, 500, and 50 ppm solutions in the three dielectric fluids. The result of greatest practical interest was the observation that the yield of PCDF, expressed as ug PCDF/g mixture pyrolyzed, decreased by a factor of 100 or more as PCB concentration was decreased from 1,000,000 to 5000 ppm, and that yields decreased monotonically as PCB concentrations were lowered from 5000 to 50 ppm. Much larger decreases were observed as TCB concentrations were lowered to 5000 ppm; in fact, no PCDF or PCDD could be detected in pyrolysates of 5000, 500, or 50 ppm solutions. An alternative way to discuss the PCB and TCB results is in terms of PCDF or PCDD yield per gram of PCB or TCB pyrolyzed. This mode of interpretation, though of less practical significance, can facilitate understanding of the mechanisms of PCDF and PCDD formation. On this basis, PCDF yields are only moderately influenced by

dilution of Aroclor 1254 from 1,000,000 to 5000 ppm with mineral oil or silicone oil. The data contain equivocal evidence for improved yields from 50 ppm Aroclor 1254 solutions in mineral oil as compared to 500 or 5000 ppm, and clearer evidence for this phenomena in the corresponding silicone oil solutions. This result implies the existence of a destructive pathway for PCB and/or PCDF that is higher than first order for PCB. Interestingly, no evidence for PCB conversion to PCDF was noted in the 5000 ppm TCE solutions; destruction of pre-existing PCDF in the PCB appeared predominant. The TCB data, expressed again as yield PCDF or PCDD per gram of TCB pyrolyzed, suggests that at 5000 ppm concentrations, the rate or yield limiting step must be kinetically bimolecular in TCB concentration.

Combustion experiments were performed by motorized syringe-drive introduction of solution into a natural gas fueled flame mounted in a one meter horizontal quartz tube itself mounted in a thermostatically controlled oven. The entire gas flow was drawn through a series of traps arranged to ensure complete removal of organics. Some interesting observations include the fact that combustion of TCE alone can form very small amounts (ng/ml) of dibenzofurans. (The pyrolysis of TCE itself at 650°C also formed low amounts of PCDFs.) The solvent/chloroorganic combination that was most prone to PCDF formation during these combustion experiments was Aroclor 1254 in TCE. Aroclor 1254 in TCE, mineral oil, or silicone oil gave yields of PCDF (expressed as ug PCDF/g PCB) which varied only modestly, if at all, over the 5000-50 ppm concentration range. Yields from combustion of 5000 ppm solutions of TCBs in mineral oil, hexane, or silicone oil were markedly lower than obtained from the corresponding PCB solutions, again suggesting the rate or yield limiting step may be second order in TCB and thus sharply affected by dilution. In contrast, TCB in TCE forms considerable PCDF on combustion, probably resulting from reaction of one TCB derived molecule with multiple TCE-derived molecules.

The observation that combustion of PCB or TCB in TCE forms higher yields of PCDFs than the corresponding combustion in mineral oil or silicone oil is in contrast to results obtained during pyrolysis. In those experiments, pyrolysis of Aroclor 1254 in mineral oil or silicone oil clearly gave higher yields than the corresponding reaction in TCE. This dichotomy illustrates what may be the most important result of these studies. Qualitatively very different results can be obtained from a particular chloroorganic/dielectric combination depending on the experimental parameters and heating regimen used.