

Reactivity of Chloroacetamides Toward Sulfide + Black Carbon: Insights from Structural Analogues and Dynamic NMR Spectroscopy

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Chloroacetamides are commonly used in herbicide formulations, and their occurrence has been reported in soils and groundwater. However, how their chemical structures affect transformation kinetics and pathways in the presence of environmental reagents such as hydrogen sulfide species and black carbon has not been investigated. In this work, we assessed the impact of increasing Cl substituents on reaction kinetics and pathways of six chloroacetamides. The contribution of individual pathways (reductive dechlorination vs. nucleophilic substitution) to the overall decay of selected chloroacetamides was differentiated using various experimental setups; both the transformation rates and product distributions were characterized. Our results suggest that the number of Cl substituents affected reaction pathways and kinetics: trichloroacetamides predominantly underwent reductive dechlorination whereas mono- and dichloroacetamides transformed via nucleophilic substitution. Furthermore, we synthesized eight dichloroacetamide analogs ($\text{Cl}_2\text{CHC}(=\text{O})\text{NRR}'$) with differing R groups and characterized their transformation kinetics. Dynamic NMR spectroscopy was employed to quantify the rotational energy barriers of dichloroacetamides. Our results suggest that adsorption of dichloroacetamides on black carbon constrained R groups from approaching the dichloromethyl carbon and subsequently favored nucleophilic attack. This study provides new insights to better predict the fate of chloroacetamides in subsurface environments by linking their structural characteristics to transformation kinetics and pathways.