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Several chlorinated org. compds. (COCs) that have been detected in a wide range of human, animal, and environmental samples may be derived from natural or anthropogenic sources. To det. whether the Cl isotope ratios of these compds. could be used to differentiate sources, we investigated the chlorine isotope effect for enzyme-catalyzed chlorination. Two arom. substrates, 1,3,5-trimethylbenzene (TMB) and 3,5-dimethylphenol (DMP), were treated with a chloroperoxidase isolated from the fungus Caldariomyces fumago. A kinetic isotope effect (KIE) (in terms of k35/k37) was calcd. to be 1.012 for TMB and 1.011 for DMP. A similar reaction, but not catalyzed, with hypochlorite yielded a much smaller KIE. These results indicate that a substantial KIE exists for this process. Furthermore, natural COCs synthesized by this enzymic pathway may have Cl isotope ratios that will be easily distinguished from anthropogenic COCs.