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Catalytic Dehalogenation of sp^2 C−F and C−Cl Bonds in Fluoro- and Chloroalkenes

Alicia A. Peterson and Kristopher McNeill*

Department of Chemistry, University of Minnesota, 207 Pleasant Street SE, Minneapolis, Minnesota 55455

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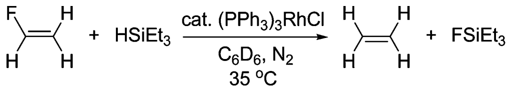
Summary: Catalytic dehalogenation of fluorinated and chlorinated ethylenes by $(PPh_3)_3RhCl$ *in the presence of* Et_3SiH *at 35 °C is described, and product identity and kinetic parameters were determined. This system has an intramolecular preference for Cl over F removal, an intermolecular preference for F- over Cl-containing alkenes, and a strong preference for sp*^{2} *over sp*^{3} *carbon−halogen bonds. Both the substitution pattern and the substituent identity are important in determining the rate of the dehalogenation.*

Interest in transition metal promoted C−F bond activation has been increasing in recent decades, mirroring the growth of fluorocarbons in new materials, pharmaceuticals, and other applications.[1] While there have been substantial advances in C−F activation reactions, catalytic systems remain rare.[2−7] Since the initial report, in 1994, of catalytic C−F activation by Aizenberg and Milstein,[2] phosphinorhodium complexes have emerged as promising homogeneous defluorination catalysts, being active toward fluorinated arenes[2−4] and alkenes.[5] In these studies, H_2 and various silanes have been employed as reducing agents, and alkyl and aryl phosphines have been used as ancillary ligands. We became interested in these systems due to their apparent preference for sp^2-hybridized C−F bonds and our interest in haloalkene dehalogenation.[8] To this end, we initiated a study of phosphinorhodium-catalyzed dehalogenation of simple mono- and disubstituted fluoro- and chloroalkenes. These substrates are important to study, not only for their environmental relevance but also because they represent elementary sp^2-hybridized structures that may yield valuable mechanistic information.

Treatment of vinyl fluoride (20 mM in C_6D_6) with Et_3SiH (125 mM) and a catalytic amount of $(PPh_3)_3RhCl$ (2.4 mM) at 35 °C leads to complete defluorination in 50 min (eq 1). The initial products are Et_3SiF, Et_3SiCl, and ethylene. The yield of this process is nearly quantitative, as 90% of the C_2 mass is accounted for as ethylene, as determined by ^1H NMR integration versus an internal standard, *p*-xylene. With extended reaction times, ethylene is consumed, yielding $Et_3SiCHCH_2$, Et_4Si, ethane, and butenes. If fluoride is transferred to the rhodium during the course of the reaction, $(PPh_3)_3RhF$ may be an intermediate. While not proof of its intermediacy, it is noteworthy that the defluorination reaction can be performed starting with $(PPh_3)_3RhF$, which was prepared independently.[9] No reaction is observed when vinyl fluoride is treated with either Et_3SiH or $(PPh_3)_3RhCl$ alone.



(1)

Under identical reaction conditions, vinyl chloride undergoes dechlorination to yield ethylene.[10] Mixed fluorochloroethylenes also undergo dehalogenation. Reaction of 1,1-chlorofluoroethylene proceeds rapidly, giving complete dehalogenation in 120 min at 35 °C. The dechlorination product, vinyl fluoride, is observed by ^1H NMR as an intermediate during the reaction. No vinyl chloride was observed, indicating that *intramolecular* competition favors chloride over fluoride elimination. Dehalogenation of a mixture of 1,2-chlorofluoroethylenes shows similar selectivity. As with 1,1-chlorofluoroethylene, only vinyl fluoride is observed during the dehalogenation of the 1,2-chlorofluoroethylene mixture, reinforcing the conclusion that intramolecular competition favors chloride loss in this system.

To further characterize this fundamental C−F bond activation process, a study of the reaction kinetics was undertaken. The

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* E-mail: mcneill@chem.umn.edu.

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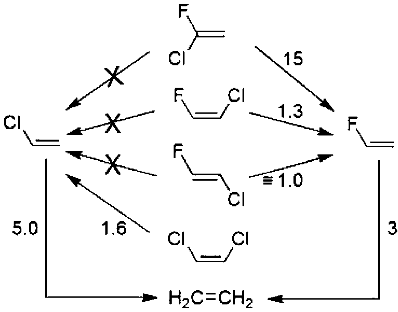


Figure 1. Relative rate constants of dehalogenation for chlorinated and fluorinated ethylenes and their subsequent reaction products. Values were determined from loss of substrate over time using ^{1}H NMR at 35 °C and are relative to the rate of dehalogenation for *trans*-1,2-chlorofluoroethylene ($k_{obs} = 1.7 \times 10^{-5}$ s^{-1}). Each sealable NMR tube contained substrate (20−30 mM), catalyst ($(PPh_3)_3RhCl$, 2.4 mM), Et_3SiH (125 mM), and internal standard (*p*-xylene, 3.3 mM) in C_6D_6.

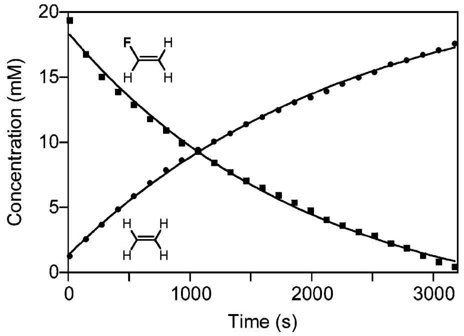


Figure 2. Vinyl fluoride degradation by $(PPh_3)_3RhCl$ (2.4 mM) and Et_3SiH (125 mM) at 35 °C and the subsequent appearance of ethylene as a reaction product. Curves represent nonlinear first-order decay and growth fits to the data for vinyl fluoride and ethylene, respectively.

kinetic experiments were conducted in a temperature-controlled NMR probe under the same conditions described above. Concentrations of the reactants and products were determined by integration of the ^{1}H NMR resonances relative to those of the internal standard (*p*-xylene). All substrates exhibited pseudo first-order kinetics, and the relative rate constants of substrate loss are summarized in Figure 1. A representative set of kinetic data for vinyl fluoride degradation is shown in Figure 2. The reaction was performed with a catalyst loading as low as 0.5%. The measured dehalogenation rate constant varies linearly with catalyst concentration.

Given the generally lower reactivity of C−F bonds compared to C−Cl bonds, it was surprising to find vinyl fluoride to be the fastest substrate, with a dehalogenation rate 6 times that of vinyl chloride. This *intermolecular* kinetic preference for the fluorinated substrate stands in contrast to the preferential C−Cl cleavage seen in chlorofluoroalkenes, the result of *intramolecular* competition. Another striking kinetic result was the much faster dehalogenation of 1,1-chlorofluoroethylene compared to 1,2-chlorofluoroethylenes, with the latter substrates taking hours instead of minutes to complete.

The inherently lower reactivity of 1,2-dihaloalkenes compared to 1,1-dihaloalkenes in this system is also seen with *cis*-1,2-dichloroethylene and 1,1-dichloroethylene. Both substrates were found to yield vinyl chloride as an intermediate. No isomerization of the *cis*-1,2-dichloroethylene to *trans*-1,2-dichloroethylene was observed during the dechlorination. Similar to the fluorochloroethylenes, 1,1-dichloroethylene was dechlorinated faster than *cis*-1,2-dichloroethylene at 35 °C. Taken together, the results indicate that the substitution pattern is potentially as important as the substituent identity in determining the dehalogenation rate.

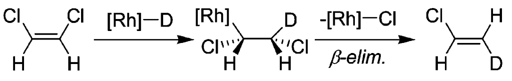
This system shows a marked preference for sp^2-hybridized C−X bonds versus sp^3-hybridized bonds. For example, many of the kinetic runs were conducted with a small amount of CH_2Cl_2 present due to cocrystallization with $(PPh_3)_3RhCl$. No decay of the CH_2Cl_2 peak area was observed during the dehalogenation of sp^2-hybridized C−X bond containing substrates. The same lack of reactivity was found when CH_2Cl_2 was employed alone as a substrate, in the absence of any potential competitors. Similarly, 1,1,2-trichloroethane and 1-fluorooctane show no dehalogenation under the reaction conditions. The lack of reactivity with sp^3 C−F bonds is notable, as it indicates that the reactive species is not Et_3Si^+, which has been shown to catalytically and selectively defluorinate sp^3 C−F bonds.[7]

Not all sp^2-hybridized C−F bonds are reactive; fluorobenzene shows no defluorination under these conditions. Other groups working with closely related systems have also noted the recalcitrant nature of fluorobenzene.[2−4] Young and Grushin were able to activate the C−F bond of 1-fluoronaphthalene using $(PCy_3)_2Rh(H)Cl_2$ under more forcing conditions (95 °C and 80 psi H_2) than employed in this study.[4]

The catalytic defluorination system using $(PPh_3)_3RhCl$ as a precatalyst in the presence of Et_3SiH is defined by three notable features: fluoroalkenes react faster than fluoroarenes and fluoroalkanes; vinyl fluoride reacts faster than vinyl chloride; and, (in an apparent contradiction) when both fluoro and chloro substituents are present, such as in 1,1-chlorofluoroethylene, the chloro substituent is removed preferentially. These facts suggest a mechanism that has (at least) two steps, rate-determining insertion of the alkene into a metal−hydride or metal−silyl bond followed by cleavage of the C−X bond. Such a general scheme would account for the enhanced reactivity of the vinyl fluoride owing to the small steric profile and good π-donating ability of the fluoro substituent. It also allows for an intramolecular preference of C−Cl cleavage over C−F cleavage, if chloride is a better leaving group than fluoride in this system, as long as it occurs after the rate-determining step.

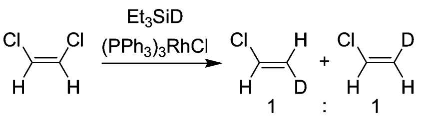
While the reaction mechanism has not been established, we have been able to exclude two leading candidates: insertion/β-halide elimination and hydrosilation forming haloalkylsilane intermediates.

A two-step process that involves insertion of a haloalkene into the Rh−H bond to yield a β-haloalkyl rhodium species followed by β-halogen elimination predicts stereospecific placement of the incoming hydride. The example of Rh−D and 1,2-*cis*-dichloroethylene is shown in eq 2.



(2)

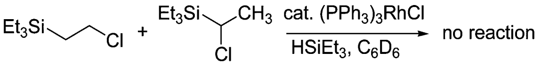
When 1,2-*cis*-dichloroethylene is treated with Et_3SiD and $(PPh_3)_3RhCl$, a 1:1 mixture of *E* and *Z* 1-chloro-2-deuteroethylene is produced, even at early reaction times (eq 3).



(3)

This is strong evidence against the simple insertion/β-elimination mechanism (eq 2).

A second mechanism involoves catalytic hydrosilation of the vinyl halides to give haloalkysilanes. These haloalkylsilanes would then eliminate Et_3SiX and the dehalogenated alkene. Independent preparation of α- and *β*-chloroethylsilane, the hydrosilation product of vinyl chloride, was accomplished by chlorinating Et_4Si using Cl_2 with PCl_5 catalyst under ultraviolet light.[11] Subjecting this mixture to the catalytic dehalogenation conditions ($(PPh_3)_3RhCl$, Et_3SiH, C_6D_6) resulted in no reaction up to 72 h (eq 4). The stability of these haloalkylsilanes to the reaction conditions rules out their intermediacy.



(4)

These preliminary mechanistic studies exclude mechanisms for specific substrates, *cis*-1,2-dichloroethylene and vinyl chloride, respectively, but it should be noted that it is possible that these mechanisms are operative for other substrates. Further mechanistic studies are in progress.

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Supporting Information Available: Full experimental details, $(PPh_3)_3RhCl$ kinetic order plot, table of k_{obs} values with error. This material is available free of charge via the Internet at http://pubs.acs.org.

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