HYDROGENOLYSIS OF CARBON-CHLORINE
BONDS IN AROMATIC MOLECULES

J. Tavana, M. Al-Gharrawi, M. C. Wheeler and T. J. Schwartz[*]
University of Maine
Orono, ME 04469

Abstract

Low-temperature hydrogenolysis of C-Cl bonds is an important reaction for the synthesis of certain chlorobenzenes and chlorophenols, as well as for several environmental remediation strategies. Here, we use a combination of reaction kinetics studies and microkinetic analysis to probe the Pd-catalyzed C-Cl bond cleavage in chlorobenzene (PhCl). The reaction is fractional order with respect to both PhCl and H_2 pressures, and it is negative-order with respect to HCl pressure. These reaction orders are temperature-dependent. The kinetics data are explained by a reaction sequence in which C-Cl bond scission is rate-controlling and where both PhCl and Cl cover the catalyst surface.

Keywords

Hydrogenolysis, Chloroaromatics, Microkinetic Analysis.

Introduction

The selective hydrogenolysis of C-X bonds, where X can be a carbon, oxygen, nitrogen, sulfur, or halide, such as chlorine, is an important class of reactions for producing chemicals from petroleum feedstocks. In particular, the synthesis of certain chlorobenzenes and chlorophenols from benzene and phenol, respectively, involves the selective hydrodechlorination of polychlorinated species (Densmurs and Ratton, 2000; Krishnamurthi, 2000). This reaction is attractive not only because it provides a use for unwanted byproducts (*i.e.*, over-chlorinated benzenes or phenols) but also because it can provide access to certain isomers not obtainable by other means (*e.g.*, species chlorinated in the *meta* position).

While much research has focused on the cleavage of C-C and C-N bonds, the cleavage of C-Cl bonds shares many features with these better-studied reactions. According to Sinfelt, the hydrogenolysis of ethane, methylamine, and methyl chloride all proceed by a similar mechanism, and in all three cases the rate-controlling step is the cleavage of the C-X bond (Sinfelt, 1991). However, the literature describing the hydrodechlorination of aromatic molecules is somewhat murkier, and several competing mechanisms have been proposed (Keane and Murzin, 2001), not all of which agree with what is known about the better-understood aliphatic systems. Inspired by this discrepancy, we have performed reaction kinetics studies and microkinetic analysis to elucidate the mechanism by which the C-Cl bond in chlorobenzene (PhCl) is cleaved.

Methods

Reactions were carried out in a glass CSTR operated as a Carberry reactor. The catalyst was suspended on the impellor in mesh baskets. PhCl was fed from a syringe pump into a flowing stream of either hydrogen or helium, controlled by metering valves. Product concentrations were measured by GC. HCl was scrubbed from the outlet gas by bubbling through water saturated with NaOH. The Pd/C catalysts were prepared by incipient wetness impregnation of carbon with an aqueous solution of palladium nitrate.

---

[*] To whom all correspondence should be addressed

Results and Discussion

The rate of benzene production was measured over a 5 wt% Pd/C catalyst, with a Pd dispersion of 8% that corresponds to 14 nm Pd nanoparticles. The reaction rate was independent of stirring speed above 300 rpm, and the Weisz-Prater criterion was 0.047, indicating are measurements are free of both internal and external mass transfer limitations. Over this catalyst, the selectivity to benzene was above 95% at 50% PhCl conversion, and the catalyst was stable for at least 50 hours of time-on-stream. As shown in Figure 1, the rate is nearly first-order with respect to PhCl pressure at 353 K, although the order decreases to zero at 323 K. In contrast, the rate is half-order with respect to H_2 pressure irrespective of temperature. The rate is also inhibited by the presence of HCl, and at 353 K the rate is inverse first-order with respect to HCl pressure.
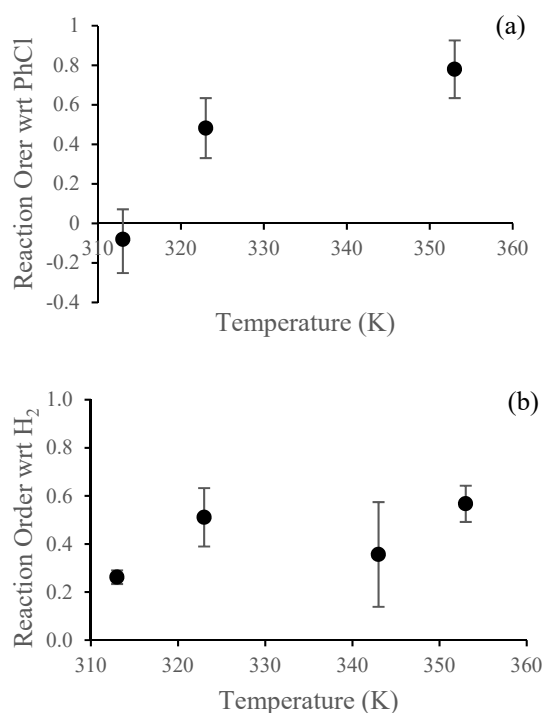

Figure 1. Influence of temperature on reaction orders with respect to a) PhCl and b) hydrogen. Reaction conditions: PhCl conversion = 50%, WHSV = 1-6 h^{-1}.

The reaction was carried out in both pure H_2 and pure D_2, and the resulting kinetic isotope effect was observed to be 1.02 thereby indicating that C-H and Cl-H bond formation are not rate-controlling. Along the same lines, Ribeiro and coworkers have observed that carbon-halide bond scission should be rate controlling, and the hydrogenolysis rate scales linearly with the strength of the C-X bond being cleaved (Thompson, 2001). Similarly, it has been observed that the rate of C-X bond cleavage in chloroaromatics also follows a linear free energy relationship (Kraus and Bazant, 1973), suggesting that C-Cl bond cleavage is rate controlling during C-Cl hydrogenolysis of chlorobenzene.

$$ r = \frac{k_3 K_2 P_{PhCl}}{1 + K_2 P_{PhCl} + \dfrac{P_{HCl}}{K_5 \sqrt{K_1 P_{H_2}}}} \tag{1} $$

The reaction orders suggest that both PhCl and Cl are abundant on the catalyst surface, which can be coupled with the observation C-Cl bond cleavage is rate-controlling to obtain the rate expression shown in Eq. 1. Notably, this rate expression is consistent with that advanced by Sinfelt (Sinfelt, 1991). A microkinetic analysis was performed, wherein the rate and equilibrium constants were decomposed into enthalpies and entropies, which were constrained based on the literature. Only three parameters required fitting, and the resulting model captures the trends in the experimental data, suggesting this mechanism is accurate for C-Cl hydrogenolysis in aromatic molecules.

Conclusions

We have used a combination of reaction kinetics and kinetic isotope effect measurements, linear free energy relationships, and microkinetic analysis to evaluate Pd-catalyzed C-Cl hydrogenolysis in chlorobenzene. These analyses suggest that C-Cl bond scission is rate-controlling, and both PhCl and Cl are abundant on the Pd surface under reaction conditions, which is consistent with a broad range C-X hydrogenolysis reactions for a variety of molecules.

Acknowledgments

References

Densmurs, J.-R., Ratton, S. (2000). Chlorophenols. In *Kirk-Othmer Encyclopedia of Chemical Technology*. John Wiley & Sons.

Keane, M. A., Murzin, D. Y. (2001). A kinetic treatment of the gas phase hydrodechlorination of chlorobenzene over nickel/silica: beyond conventional kinetics. *Chem. Eng. Sci. 56*, 3185.

Krishnamurti, R. (2000). Chlorinated Benzenes. In *Kirk-Othmer Encyclopedia of Chemical Technology*. John Wiley & Sons.

Kraus, M., Bazant, V. (1973) In *Catalysis: Proceedings of the Fifth International Congress*. Elsevier. Vol. 2, 1073.

Sinfelt, J. H. (1991). Catalytic Hydrogenolysis on Metals. *Catal. Lett.*, *9*, 159.

Thompson, C. D., Rioux, R. M., Chen, N., Ribeiro, F. H. (2001). Turnover Rate, Reaction Order, and Elementary Steps for the Hydrodechlorination of Chlorofluorocarbon Compounds on Palladium Catalysts. *J. Phys Chem. B*, *104*, 3067.