Decomposition of Carbocations by Sterically Hindered Pyridines (Executive Summary)

Sterically hindered pyridines (SHPs) are derivatives of pyridine with bulky substituents (*i.e.* *t*-butyl) in the 2 and 6 positions (Figure 1). The two large/bulky *t*-butyl substituents sterically shield the basic nitrogen (acting like 2 molecular walls) and allow only the smallest of acidic species access to the ring nitrogen. In comparison to pyridine the reactivity of SHPs are very specific and the latter have long been considered non-nucleophilic (*i.e.* non-nucleus loving) bases that react preferentially with hydrogen ion (*i.e.* proton, H^+).[1] This behavior has earned SHPs the nickname *proton trap*. SHPs have been used successfully to determine if H^+ is essential in a chemical reaction; if a process is dependent on H^+ introduction of a SHP will thwart reaction. Use of SHPs as a diagnostic for H^+ mediated chemistry is dependent on the assumption that SHPs are unreactive towards other acidic species (*e.g.* carbocations). In most cases this assumption holds true and SHPs have been used with great success in the determination of reaction mechanisms. SHPs have been used to prevent both protic initiation and chain transfer (processes involving H^+) in carbocationic polymerization and impart living characteristics to a given polymerization.[2] Some researchers[3] have witnessed behavior that suggests SHPs can react with species other than H^+ but have not been able to provide conclusive evidence that this is the case.

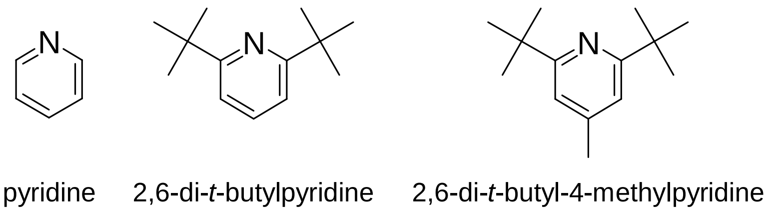

Figure 1. Pyridine and Common SHP Derivatives

While at The University of Akron, Dr. Lewis[4] found that the $[\text{cumyl}]^+$ $[1,2\text{-}C_6F_4\{B(C_6F_5)_2\}_2\ (\mu\text{-Cl})]^-$ ion pair (Figure 2) was consumed instantaneously when it was generated at -80 °C in the presence of the SHP, 2,6-di-*t*-butyl-4-methylpyridine. This was astonishing as the $[\text{cumyl}]^+$ $[1,2\text{-}C_6F_4\{B(C_6F_5)_2\}_2\ (\mu\text{-Cl})]^-$ ion pair is normally stable under these conditions in the absence of 2,6-di-*t*-butyl-4-methylpyridine and that the reaction products could readily be explained by assuming that 2,6-di-*t*-butyl-4-methylpyridine is able to decompose cumyl carbocation by β-H^+ extraction. Dr. Lewis[5] theorized that this behavior could be attributed to the $[1,2\text{-}C_6F_4\{B(C_6F_5)_2\}_2\ (\mu\text{-Cl})]^-$ counteranion of the ion pair $[\text{cumyl}]^+$ $[1,2\text{-}C_6F_4\{B(C_6F_5)_2\}_2\ (\mu\text{-Cl})]^-$. The $[1,2\text{-}C_6F_4\{B(C_6F_5)_2\}_2\ (\mu\text{-Cl})]^-$ counteranion is classified as a weakly coordinating anion and it

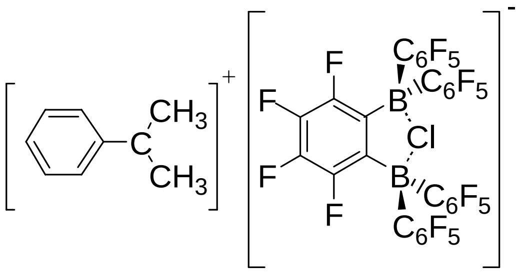

Figure 2. $[\text{cumyl}]^+$ $[1,2\text{-}C_6F_4\{B(C_6F_5)_2\}_2\ (\mu\text{-Cl})]^-$ Ion Pair

is *loosely* associated with the cumyl carbocation. Since the $[\text{cumyl}]^+$ $[1,2\text{-}C_6F_4\{B(C_6F_5)_2\}_2(\mu\text{-Cl})]^-$ ion pair is not bound together tightly 2,6-di-*t*-butyl-4-methylpyridine is able to approach the cumyl carbocation close enough to allow decomposition to occur. Subsequent investigation at The University of Akron provided additional spectroscopic evidence that indeed this is the case.[6] Previously investigators were not able to witness such behavior as their systems contained traditional counteranions that blocked the approach of SHP to the carbocation preventing decomposition from occurring. In conclusion, if a carbocation is sufficiently separated from its counteranion it can undergo reaction with a SHP.[7]

References

1. (a) Brown, H.C.; Kanner, B. *J. Am. Chem. Soc.* **1953**, *75*, 3865. (b) Brown, H.C.; Kanner, B. *J. Am. Chem. Soc.* **1966**, *88*, 986. (c) Anderson, A.G.; Stang, P. J. *J. Org. Chem.* **1976**, *41*, 3034. (d) Forbus, T.R. Jr.; Martin, J.C. *J. Org. Chem.* **1979**, *44*, 313.
2. (a) Balogh, L.; Faust, R. *Polym. Bull.* **1992**, *28*, 367-374. (b) Gyor, M.; Wang, H. C.; Faust, R. *J. Macromol. Sci., Chem.* **1992**, *A29* (8), 639-653. (c) Fodor, Z.; Bae, Y.C.; Faust, R. *Macromolecules* **1998**, *31*, 4439-4446. (d) Hadjikyriacou, S.; Acar, M.; Faust, R. *Macromolecules* **2004**, *37*, 7543-7547.
3. (a) Guhaniyogi, S.C.; Kennedy, J.P.; Ferry, W.C. *Macromol. Sci., Chem.* **1982**, *A18* (1), 25-37. (b) Nuyken, O.; Pask, S.D.; Walter, M. *Polym. Bull.* **1982**, *8*, 451-455. (c) Dembinski, A.; Yagci, Y.; Schnabel, W. *Polymer* **1993**, *34* (17), 3738-3740. (d) Storey, R.; Curry, C.L. *ACS Div. Polym. Chem., Polym. Prepr.* **1999**, *40* (2), 954-955.
4. Lewis, Stewart P., Ph.D. Dissertation, The University of Akron, 2004.
5. Lewis, S. P. *An Abbreviated Summary of Findings for Solution and Aqueous Suspension/Emulsion Polymerization of Isobutylene Coinitiated by* $1,2\text{-}C_6F_4[B(C_6F_5)_2]_2$; www.stewartstechnologies.com, 2005.
6. (a) Jianfang, C.; Lewis, S. P.; Kennedy, J. P.; Collins, S. *Macromolecules*, **2007**, *40*(21), 7421-7423. (b) Jianfang, C.; Lewis, S. P.; Collins, S.; Sciarone, T. J. J.; Henderson, L. D.; Chase, P. A.; Irvine, G. J.; Piers, W. E.; Elsegood, M. R. J.; Clegg, W. *Organometallics*, **2007**, *26*, 5667-5679.
7. The degree of association for a given ion pair is a complex composite of the degree of counteranion nucleophilicity and its solubility in a given system. The important implications of this statement will be demonstrated at a future date by Dr. Lewis.