Hinsberg reaction

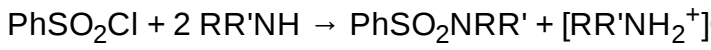
The **Hinsberg reaction** is a test for the detection of primary, secondary and tertiary amines. In this test, the amine is shaken well with Hinsberg reagent in the presence of aqueous alkali (either KOH or NaOH). A reagent containing an aqueous sodium hydroxide solution and benzenesulfonyl chloride is added to a substrate. A primary amine will form a soluble sulfonamide salt. Acidification of this salt then precipitates the sulfonamide of the primary amine. A secondary amine in the same reaction will directly form an insoluble sulfonamide. A tertiary amine will not react with the sulfonamide but is insoluble. After adding dilute acid this insoluble amine is converted to a soluble ammonium salt. In this way the reaction can distinguish between the three types of amines.[1]

Tertiary amines are able to react with benzenesulfonyl chloride under a variety of conditions; the test described above is not absolute. The Hinsberg test for amines is valid only when reaction speed, concentration, temperature, and solubility are taken into account.[2]

The Hinsberg reaction was first described by Oscar Hinsberg in 1890.[3][4]

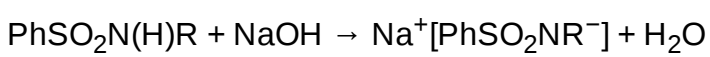
Reaction pathways

Amines serve as nucleophiles in attacking the sulfonyl chloride electrophile, displacing chloride. The sulfonamides resulting from primary and secondary amines are poorly soluble and precipitate as solids from solution:



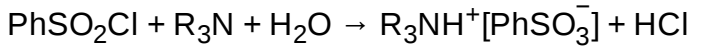
$$PhSO_2Cl + 2\ RR'NH \rightarrow PhSO_2NRR' + [RR'NH_2^+]Cl^-$$

For primary amines (R' = H), the initially formed sulfonamide is deprotonated by base to give water-soluble sulfonamide salt ($Na[PhSO_2NR]$):



$$PhSO_2N(H)R + NaOH \rightarrow Na^+[PhSO_2NR^-] + H_2O$$

Tertiary amines promote hydrolysis of the sulfonyl chloride functional group, which affords water-soluble sulfonate salts.



$$PhSO_2Cl + R_3N + H_2O \rightarrow R_3NH^+[PhSO_3^-] + HCl$$

External links

- Laboratory procedure: science.csustan.edu (https://web.archive.org/web/20090204194501/http://science.csustan.edu/almy/3022/UnkABN.htm)

References

1. "The systematic identification of organic compounds" 4th ed. by Ralph L. Shriner, Reynold C. Fuson, and David Y. Curtin. John Wiley & Sons, Inc., New York, 1956. doi:10.1002/jps.3030450636 (https://doi.org/10.1002%2Fjps.3030450636) and more recent editions.
2. Gambill, C. R. "Benzenesulfonyl chloride does react with tertiary amines. The Hinsberg test in proper prospective". *Journal of Chemical Education*. **49**: 287. Bibcode:1972JChEd..49..287G

(https://ui.adsabs.harvard.edu/abs/1972JChEd..49..287G). doi:10.1021/ed049p287 (https://doi.org/10.1021%2Fed049p287).
3. O. Hinsberg: *Ueber die Bildung von Säureestern und Säureamiden bei Gegenwart von Wasser und Alkali*, in: *Ber. Dtsch. Chem. Ges.* **1890**, *23*, 2962–2965; doi:10.1002/cber.189002302215 (https://doi.org/10.1002%2Fcber.189002302215)
4. O. Hinsberg, J. Kessler: *Ueber die Trennung der primären und secundären Aminbasen*, in: *Ber. Dtsch. Chem. Ges.* **1905**, *38*, 906–911; doi:10.1002/cber.190503801161 (https://doi.org/10.1002%2Fcber.190503801161)
