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EVIDENCE FOR PHENYL CATION AS AN INTERMEDIATE IN NUCLEOPHILIC DISPLACEMENTS ON BENZENEDIAZONIUM SALTS[1,2]

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Displacements on $C_6H_5N_2^+$ in solution in the absence of strong bases, reducing agents or light proceed by rate-determining cleavage to singlet $C_6H_5^+$. The following evidence taken collectively disproves the bimolecular mechanisms favored since 1969.[3] In hydrolysis in aqueous solution at 25°, only unrearranged products are obtained and less than 0.05% incorporation of D from solvent D_2O occurs, showing that benzyne processes do not occur to a significant extent. The low selectivity between nucleophiles ($k_{Br^-}/k_{H_2O} = 6$) nevertheless requires a highly reactive intermediate. In the hydrolysis of $C_6H_5N_2^+$, the high entropy of activation (+10.5 e.u.) and the constancy of k_1 (within 4%) from H_2O to D_2O prove that H_2O is not involved as a nucleophile in the rate-determining step. The constancy of k_1 (within 10%) in solutions as diverse as 14 to 21 M H_2SO_4, 100% CH_3CO_2H and 100% CH_2Cl_2 is in accord with a common rate-determining step over this whole range of solvents.

Deuterium isotope effects, k_H/k_D, are 1.22 ± 0.01 for each o-position, 1.08 ± 0.01 for each m-position and 1.02 for the p-position in dediazoniations of $C_6H_5N_2^+BF_4^-$ in aq H_2SO_4, 100% CH_3CO_2H or CH_2Cl_2 solutions at 25°. These ortho effects are the largest secondary aromatic hydrogen isotope effects yet observed. The lower effect for benzenediazonium-2,4,6-d_3 ion with 3,5-dimethyl substituents (1.48 with, 1.52 without) demonstrates that hyperconjugative delocalization of positive charge onto o- and m-hydrogens in the transition state, rather than relief of strain, is the source of these kinetic isotope effects.

The α-nitrogen isotope effect, k_{14}/k_{15}, in dediazoniation of 0.1 M $C_6H_5N_2^+BF_4^-$ in 1% H_2SO_4 solution at 25° is unusually high, 1.0384 ± 0.0010, as deduced from the β-N isotope effect of 1.0106 ± 0.0003 for the enriched β-^{15}N compound and the over-all isotope effect of 1.0245 ± 0.0005 for the normal compound. Use of an independent method of analysis for the nitrogens in $C_6H_5N_2^+$ confirms the conclusion of Lewis, Insole and Holliday[4] that its rearrangement is a minor reaction (2.5%) under these conditions.

The Schiemann reaction ($ArN_2^+BF_4^- \rightarrow ArF$) does not require dissociation of BF_4^- to F^-. The step that forms fluoroarene is a direct reaction of the BF_4^- ion. This is demonstrated by insensitivity to excess BF_3 concentration of the ratio of products, ArF/ArCl, from p-t-butylbenzenediazonium fluoborate in methylene chloride solution at 25°.

p-Substituent effects on hydrolytic rates (p-OCH_3, CH_3, $C(CH_3)_3$, H, C_6H_5, Cl, NO_2) in aqueous solution at 25° can be dissected into nearly equal field (predominantly transition state) and resonance (predominantly reactant) contributions by an analysis using dual substituent constants (previously published[5]) with a correlation coefficient of 0.992, although analysis using the Hammett $\rho\sigma$ equation, i.e., with only a single set of substituent constants, yields a correlation coefficient worse than zero (imaginary).

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