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Studies of Solvolyses of 1,4-Bis(4-Benzodioxan-6-yl)Sulfonyl Chloride by Extended Grunwald-Winstein Equation

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First published: 09 November 2015

<https://doi.org/10.1002/bkcs.10573>

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Abstract

The rate constants of solvolysis of 1,4-benzodioxan-6-sulfonyl chloride ($\text{C}_6\text{H}_7\text{ClO}_4\text{Cl}$, **1**) were determined by a conductivity technique. These rate constants of **1** in 28 different solvents correlated well with the extended Grunwald-Winstein equation. The ρ (1.00) and m (0.59) values support an $\text{S}_{\text{N}}2$ reaction pathway having a similar transition state structure to that of the benzenesulfonyl chloride (**2**, $\rho = 1.10$, $m = 0.61$) reaction. This interpretation is further supported by the activation parameters, *i.e.*, relatively small positive ΔH^\ddagger (8.9 to 15.5 kcal/mol) and large negative ΔS^\ddagger (–27.3 to –49.2 cal/mol/K) values, and the solvent kinetic isotope effect (1.62). The Kivinen's n values ($n = 0.03$ in methanol, 0.04 in ethanol) obtained in binary solvents were consistent with the proposed bimolecular reaction mechanism.

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