

**Methyl-substituted allyl cations. A comparison of experimental stability, rotational barrier, and solvolysis data with ab initio calculations.** Mayr, Herbert; Foerner, Wolfgang; Schleyer, Paul von Rague.

### **Abstract**

Three sources of quant. data for methyl-substituted allyl cations are available exptl.: gas phase heats of formation, rotational barriers in soln., and rates of solvolysis. NMR chem. shifts also provide an index of charge distribution. All these lines are drawn together in comparison with results of STO-3G ab initio MO calcns. performed on planar and perpendicular methyl-substituted allyl cations. Sequential substitution of the terminal positions by one, two, three, and four Me groups stabilizes allyl cations electronically by 17, 15, 13, and 11 kcal/mol., resp.; a Me group on the central carbon has a much smaller stabilizing effect (.apprx.5 kcal/mol). The steric strain for the 1st endo-Me group was 3 kcal/mol, whereas a second endo-Me experiences a somewhat greater strain of 5 kcal/mol. Allyl solvolysis rates correlate well with gas phase allyl cation stability data, but there is a redn. in magnitude due to solvolysis. The calcd. rotational barriers also are 4-12 kcal/mol higher than the activation free enthalpies detd. in superacid soln.; the difference provides further evidence of differential solvation effects-the more highly delocalized planar forms are solvated to a lesser extent than their rotational transition states. The rotational barrier of the parent allyl cation is predicted to be 34 kcal/mol in the gas phase but to decrease to  $23.7 \pm 2$  kcal/mol in superacid soln.