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SOLVOLYSIS OF 9-CHLOROPENTACYCLO[4.3.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]NONANE ("COATES' CHLORIDE") UNDER PRESSURE

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Summary: The title reaction at 30.00° in 80% aqueous ethanol has an activation volume of $-19\ cm^3/mol$, in sharp contrast to t-butyl chloride ($-40\ cm^3/mol$); this difference, qualitatively expected on the basis of charge delocalization, is somewhat larger than expected.

When the long search for a true, solvolytically generated nonclassical carbocation reached a successful conclusion[1] in the form of Coates' ion, a standard thereby became available against which a host of special methods and arguments used earlier in the search could be tested. Among these methods, one we had proposed[2] was a comparison of the activation volume of the solvolytic reaction under consideration with that of a closely related standard free from anchimeric participation. It was shown by Drude and Nernst[3] that as a direct consequence of Coulomb's law, charge dispersal within an ion leads to a less effective overall interaction of the ion with its medium, and hence to a diminished net interaction ("electrostriction"). This interaction is proportional to q^2, and since we may assume that half of it may be attributed to the leaving group, it follows that the formation of a nonclassical ion with charge equally distributed between equivalent sites should have an activation volume one half to three fourths of that of a classical analog. This difference was indeed encountered[2] in the exo- and endo-2-norbornyl and 5-bicyclo[3.1.0]-hexyl pairs. This conclusion was later supported by determination of the volume profiles of rapid, degenerate cation equilibrations in super-acid media.[4] Coates' ion should obviously also exhibit this phenomenon if a suitable standard can be applied.

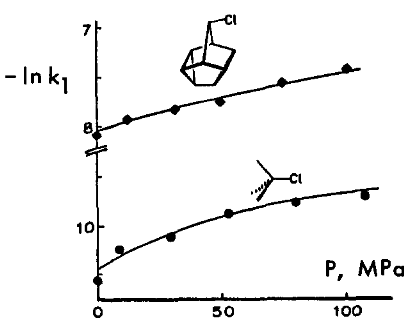

Figure. Solvolyses under pressure.

The enormous anchimeric enhancement of the rate of formation of this ion makes it impossible to compare it directly with any secondary classical analog, and we were forced to use a tertiary standard. t-Butyl chloride 1 was used, since under the same condition it has a similar rate. Coates' alcohol 2 was prepared by both the original route[1] and by $AgClO_4$-catalyzed isomerization[5] of 9-homocubanol,[6] and converted into the chloride as reported.[1] Solutions of this material (5×10^{-4} M) were solvolyzed in 80% aqueous ethanol at 30.00° by means of the conductance method previously described.[7] The result, deduced from the pressure coefficient of the first order rate constant by computer-mediated least squares fitting in the usual way, is that the value of $\Delta V^{\ddagger} = -19 \pm 2$ cm^3/mol; t-BuCl has $\Delta V^{\ddagger} = 40 \pm 3$ cm^3/mol. The correlation constants were 0.98 and 0.97, respectively, the rates were measured for several half lives at six pressures over a 150 MPa (≈1500 atm) range. The difference between these two compounds is somewhat greater than anticipated; with three equivalent sites in Coates' ion, $\Delta\Delta V^{\ddagger}$ should have been closer to 15 than to 20 cm^3/mol. If t-BuCl has a later transition state than Coates' chloride (e.g., if it is close to a loose ion-pair stage), the greater than expected difference would be accounted for. That such may indeed be the case is supported by a recent paper by Blandamer et al.[9] On the other hand, large volumes of activation are notoriously difficult to appraise accurately, and it may be that the larger than expected difference is too imprecisely known to deserve special comment.

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