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MINDO/3 Calculations of Kinetic Isotope Effects in Heterolysis of Neopentyl Alcohol

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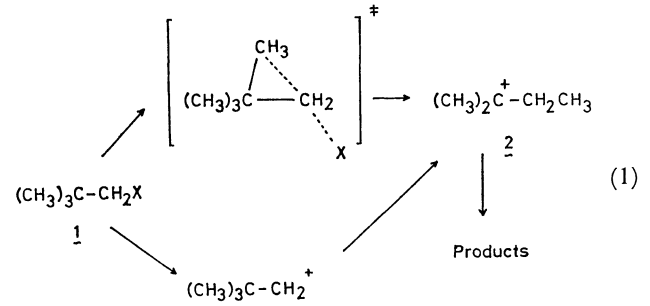
Synopsis. Geometrical optimization of the protonated neopentyl alcohol and the transition state of its heterolysis was carried out using the MINDO/3 SCF-MO method. A cyclic structure was predicted for the transition state. Agreement between the calculated and experimental values for the carbon-14 kinetic isotope effects was excellent.

Neopentyl derivatives **1**, having a fully substituted carbon atom next to the reaction center, usually give rise to substitution and elimination products to be derived from the rearranged *t*-pentyl cation **2** under solvolytic conditions (Eq. 1). The timing of this rearrangement, concerted or stepwise, has long been a subject of controversy. Pieces of evidence for and against methyl participation have been accumulated from kinetic and stereochemical researches.[1,2)]



(1)

Recent studies using kinetic isotope effect (KIE) revealed that the three methyl groups are not equivalent in the role in governing the reaction rate, only the migrating methyl group showing a large isotope effect.[3,4)] This fact, as well as the KIE data for α and β carbons, tends to support the concerted mechanism.[3,4)]

However, methyl participation or bridging is not the only possible explanation for the observed inequality in the KIE for the methyl carbons. Hyperconjugation is also strongly angular-dependent, and the idea that hyperconjugation and bridging may merge has been presented.[5)]

In order to gain an additional insight to the mechanism of neopentyl solvolysis, semiempirical SCF-MO calculations were carried out on the heterolysis process of neopentyl alcohol. Kinetic isotope effects were calculated from the molecular vibration frequencies of both the reactant and the transition state, and compared with the experimentally observed values.

Results and Discussion

Calculations were carried out by the MINDO/3 method.[6,7)] The local minimum of the protonated neopentyl alcohol $(CH_3)_3CCH_2OH_2^+$ as reactant was determined by the geometrical optimization procedure based on the gradient method.[8)] The results are shown in Fig. 1.

In order to determine the transition state geometry, the entire system at given C–O bond lengths was energetically optimized[9)] with respect to the remaining degrees of freedom. As the C–O bond was elongated, the methyl group at the *s-trans* position was caused to draw nearer to the α-carbon to form a distorted triangle. The transition state was reached when the C–C distance in question was 1.819 Å, as shown in Fig. 2.

Force constants and molecular vibration frequencies were calculated for the reactant and the transition state. The former has 51 normal frequencies, while the latter has one imaginary (430*i* cm^{-1}) and 50 normal

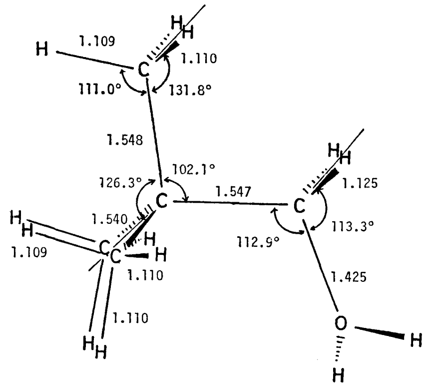


Fig. 1. Optimized structure of protonated neopentyl alcohol. Bond lengths appended are in units of Å.

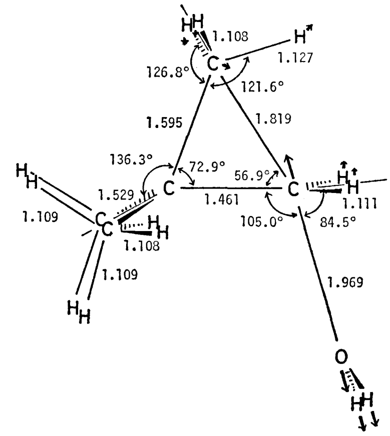


Fig. 2. Optimized structure of the transition state. Bond lengths in Å and reaction-coordinate motion are included.

Table 1. Calculated and experimental kinetic isotope effects in the heterolysis of neopentyl alcohol at 100 °C

Position[a)]	Calculated	Observed[b)]
α-^{14}C	1.084	1.073
α-D_2	0.982	1.187; 1.190
β-^{14}C	1.011	1.019
γ-^{14}C	1.022	1.037
γ-D_3	1.224	1.123
γ'-^{14}C	1.003	(1.00)[c)]
γ'-D_3	1.007	(0.95)[c)]

a) γ corresponds to the migrating methyl group while γ' to the nonmigrating groups. b) Combined data for the acetolyses of neopentyl *p*-nitrobenzenesulfonate and 2-methyl-2-adamantylmethyl brosylate (Ref. 3). c) Estimated from the data for the above-mentioned two compounds.

frequencies. The reaction-coordinate motion, *i.e.*, the mode of vibration with the imaginary frequency at the transition state, is also shown in Fig. 2. Kinetic isotope effects were calculated from the vibrational frequencies obtained.[10,11)] The results are summarized in Table 1 together with the corresponding experimental data.

As can be seen from Table 1, the carbon-14 isotope effects calculated for the various carbon atoms involved agree reasonably well with the experimental data. The results lend strong support to the concept of the concerted mechanism for the neopentyl solvolysis. As for the deuterium isotope effects, however, the agreement between calculated and observed values is found to be rather poor. These contrasting results could best be reconciled by the view that the solvation effect, not considered in the present calculations, would perhaps be more important to those hydrogen atoms which embroider the skeleton carbon atoms and hence are exposed to the solvent environment to a higher extent.

In conclusion, the present calculations support the concerted mechanism for the neopentyl solvolysis, even though there is still some question with respect to the accuracy of MINDO/3 calculations on transition states for ionic reactions.

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