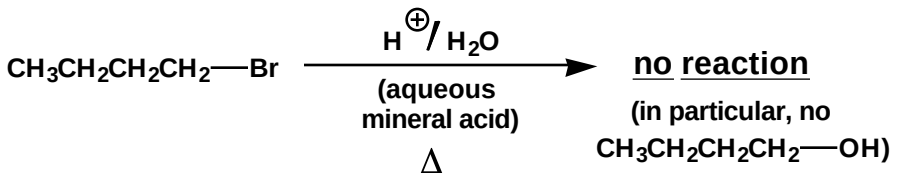
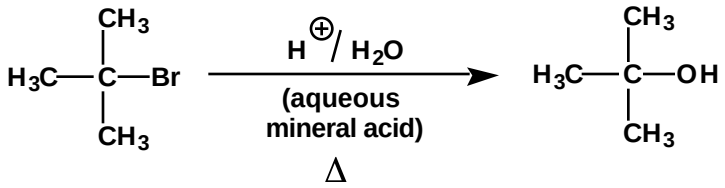
Text Related to Segment 14.01 ©2002 Claude E. Wintner

If we now consider reactions in *acidic* ionizing solvents we find — as a general rule — that primary halides are inert when exposed to such conditions. For example, when n-butyl bromide is heated in an aqueous mineral acid solution (such as aqueous HBr or aqueous H_2SO_4), no change is observed:

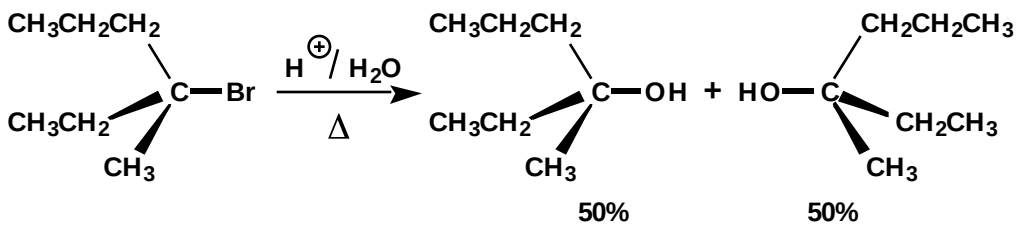


On the other hand, when tertiary-butyl bromide (t-butyl bromide) is subjected to the same conditions, the product is t-butyl alcohol:



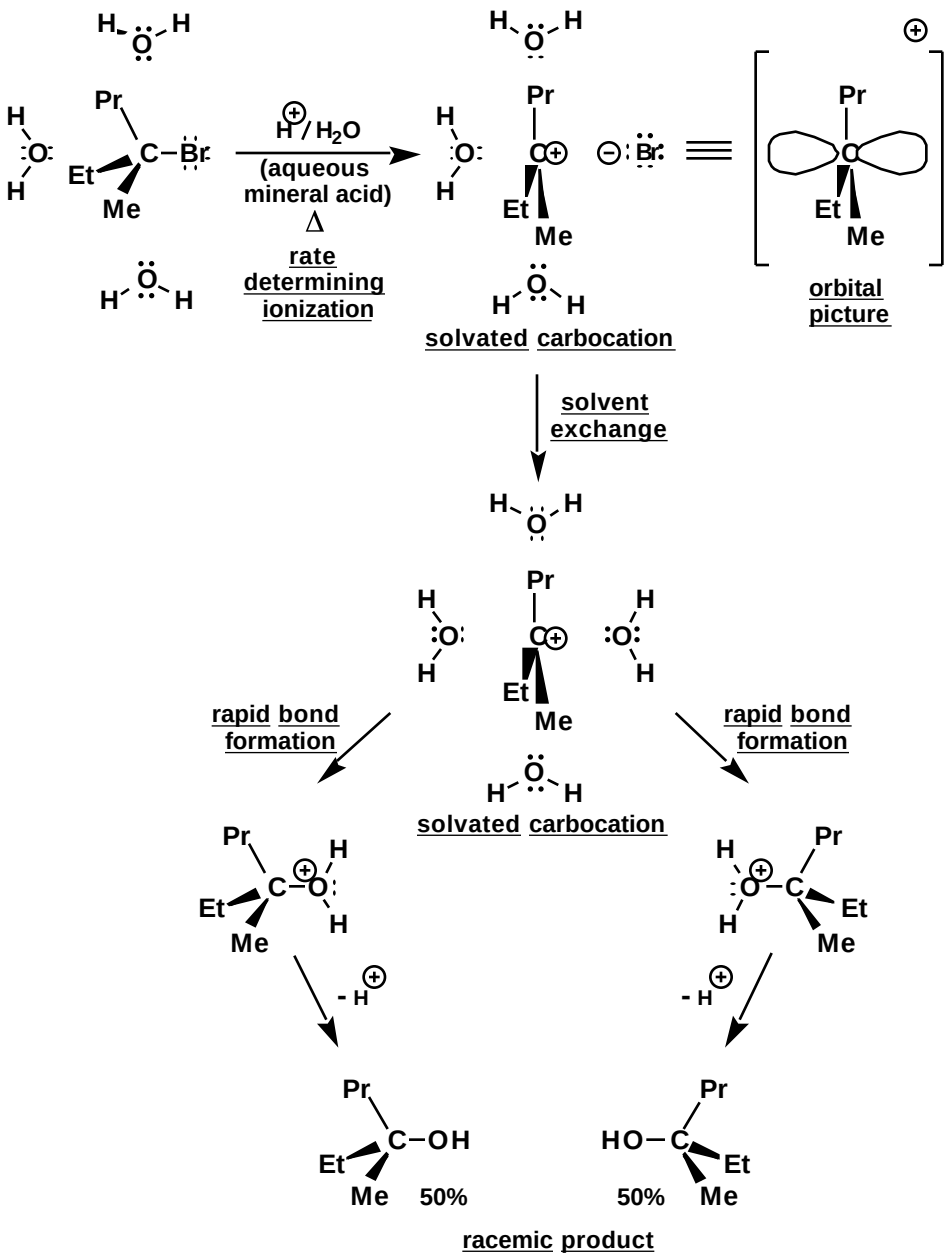
This reaction must be classified as a nucleophilic substitution, for a hydroxyl group has replaced the halide moiety; but we can feel confident that the mechanism is not bimolecular — that is, not S_N2 — since the substitution pattern at the reacting carbon center is tertiary. Indeed, our surmise is confirmed by the kinetic rate law, which is observed to be *first-order,* dependent only on the substrate concentration. In this circumstance one returns to the unimolecular mechanism already considered in Segment 13.02, but rejected in the earlier discussion on grounds that it did not predict second-order, but rather first-order, kinetics. However, in the case at hand this is precisely what we want! As regards stereochemical outcome, if the starting

material is a *resolved* chiral tertiary halide, the product alcohol is observed to be racemic:



stereochemical outcome for substitution reaction at tertiary center (first-order kinetics) is <u>racemization</u>

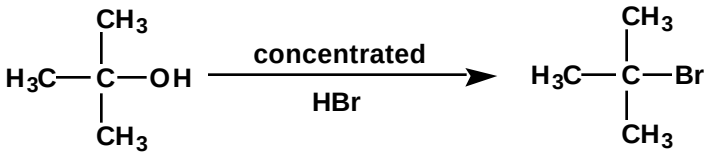
The possibility of this outcome also was raised previously, but racemization never is observed for the cases which we have classified as occurring by the S_N2 mechanism, where inversion of configuration is the necessary consequence. By the same token, the new stereochemical result in these reactions serves as *confirming evidence* for a mechanism classified instead as S_N1 (substitution, nucleophilic, unimolecular) and illustrated in the next figure. Thus, it is postulated that in a slow, rate determining ionization step the carbon-halogen bond breaks heterolytically, with the electrons going to the halogen atom. The result is a (solvated) halide anion and, as the crucial intermediate, a solvated, positively charged carbon cation, generally called a *carbocation* (in the older literature: "carbonium ion"), which may be viewed as a species having trigonal, planar sp^2 hybridization and an unfilled $2p_z$ orbital located on the central axis perpendicular to the plane. Over time it can be expected that statistical exchange factors will govern the solvation process, so that the halide anion ultimately will become "lost" in the solvent, and it will be likely that the nearest neighbors to the carbocation in solution all will be solvent molecules. The cation is presumed to collapse, via a rapid, bond-forming step with solvent nucleophiles, to form (in the case of the solvent water) oxonium ions which subsequently, upon loss of a proton to the solvent, yield the product:



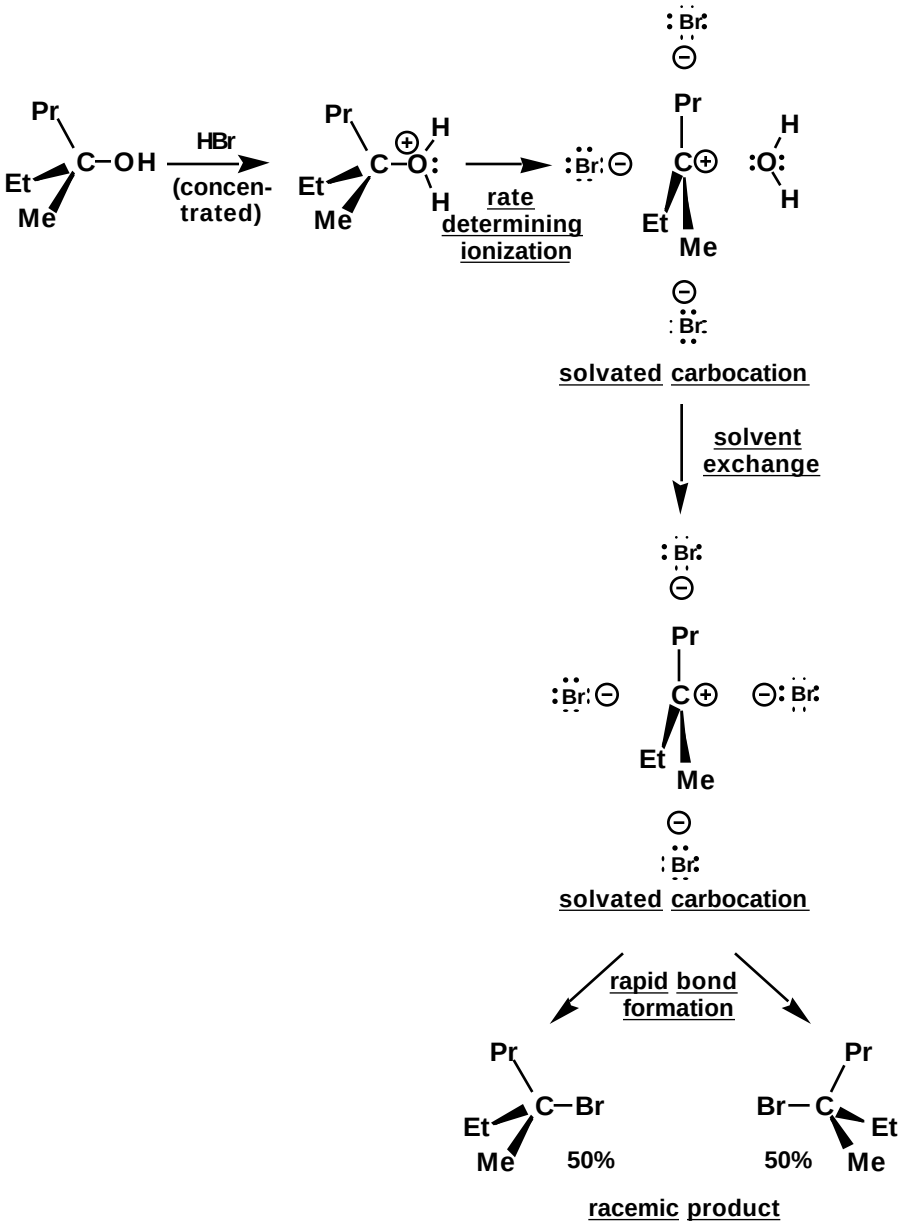
S_N1 mechanism for substitution reactions of tertiary alkyl halides in aqueous acidic ionizing solvents

Note that there is no reason to assume preferential attack by the solvent on one face or the other of the solvated planar cation; reaction should occur with equal facility at both faces, with the observed racemic result. Such a mechanism often is termed a *solvolysis* mechanism, because the solvent inevitably appears in the product.

If we treat tertiary alcohols with *concentrated* HBr, we observe the formation of the corresponding tertiary bromides:



Again the kinetics are first order, and racemization is observed in suitably constructed situations. Just a moment's reflection serves to bring us to the realization that the mechanistic route should be as delineated below — for it is, in fact, exactly the reverse of the pathway from tertiary bromides to tertiary alcohols in aqueous HBr, as already interpreted in the previous figure. Thus, the outcome of the reaction ultimately is dependent on concentration, that is, on which nucleophile — bromide ion or water — is present in excess great enough to drive the reaction one way or the other in the competition for the carbocation.



S_N1 mechanism for substitution reactions of tertiary alcohols in concentrated HBr