The adsorption and reaction of acetic acid on the Ge(001) surface are investigated by first-principles density-functional calculations. We find that the carbonyl O atom initially bonds to the down Ge atom of the buckled dimer and subsequently O-H dissociation takes place through the intradimer- or interdimer-transfer of the H atom. The resulting monodentate (MD) structure after the intradimer H-atom transfer remains stable, while that after the interdimer H-atom transfer proceeds to formation of the end-bridged (EB) bidentate structure across the ends of two adjacent dimers by forming an additional Ge-O bond on the opposite side of the H-atom transfer. It is also possible that the latter MD structure proceeds to formation of the on-top (OT) bidentate structure on a single Ge dimer, but it is kinetically difficult because of the existence of a repulsive interaction between an O lone pair and a single Ge dangling bond. The reactions for the second Ge-O bond formations in the EB and OT structures are symmetry forbidden. However, their activation barriers are significantly different from each other, showing that the Woodward-Hoffmann rule is preserved or violated depending on the reaction pathways. Our calculated energy profiles for the reaction pathways predict that, as temperature increases, the relatively less stabilized MD and EB structures are converted into the most stable OT structure, as observed by a recent scanning tunneling microscopy experiment.