Acetylated cannabinoids, such as Δ8-THC acetate and CBN acetate, have recently gained popularity due to their increased potency and current legal status. Ketene, a pulmonary toxic gas, has been observed to form from the heating of such semi-synthetic acetylated cannabinoids; however, the specific temperature dependence of ketene formation has yet to be determined. Additionally, the reaction mechanism still remains unclear for the formation of ketene from acetylated cannabinoids. In this work, we computationally simulate the reaction pathway for the formation of ketene from Δ8-THC acetate and CBN acetate under different conditions. We considered temperature dependence from 298 K to 5000 K. We also considered reactions taking place in gas and solvent phases. Our modeling was conducted with density functional theory using M062X and B3LYP functionals with the 6-311G basis set with polarization functions and diffuse functions included for heavy atoms. For the liquid phase simulations, we employed both polarizable continuum models and explicit solvent models. Our intrinsic reaction coordinate results ambiguously show that the reaction mechanism of ketene formation is concerted asynchronous, not through the four-membered ring mechanism as reported in the literature for related systems. Our temperature dependence results also show that the rate of ketene formation is highly sensitive to temperature changes. These results are confirmed in our simulations using different methodologies. This work should give a greater insight into the mechanism of ketene formation in cannabinoids and the severity of ketene exposure resulting from temperatures associated with vaping.