

Product branching of the 2-hydroxyethyl radical intermediate of the OH + ethene reaction

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The OH + ethene reaction has been studied extensively, due to the prevalence of hydroxyl radicals in atmospheric and combustion chemistry. While the abstraction pathway leading to $\text{H}_2\text{O} + \text{C}_2\text{H}_3$ is known to dominate at high temperatures, the addition pathway, which proceeds via the $\text{CH}_2\text{CH}_2\text{OH}$ radical intermediate, plays a significant role in the overall dynamics of the reaction at lower temperatures. In an effort to characterize the product branching of the OH + ethene reaction following this addition pathway, we photodissociated two halogenated precursors of the radical intermediate, $\text{BrCH}_2\text{CH}_2\text{OH}$ and $\text{BrCD}_2\text{CD}_2\text{OH}$ at 193 nm to generate highly internally excited 2-hydroxyethyl radicals.¹⁻³ Using a crossed laser-molecular beam scattering apparatus with tunable photoionization detection, and a velocity map imaging apparatus with VUV photoionization, we detected the products of the major primary photodissociation channel (Br and $\text{CH}_2\text{CH}_2\text{OH}/\text{CD}_2\text{CD}_2\text{OH}$), and of the secondary dissociation of the excited radicals.

We present results on an unexpected product channel of the 2-hydroxyethyl radical, the water + vinyl channel. The velocity distribution of the signal at $m/e = 27$ (or $m/e = 30$) allows us to identify signal from vinyl (C_2H_3 or C_2D_3) product, assigned to a frustrated dissociation toward OH + ethene followed by H- or D-atom abstraction. We compare these results to predictions from statistical transition state theory and prior classical trajectory calculations on the OH + ethene potential energy surface that evidenced a roaming channel to produce water + vinyl products. Surprisingly, the branching fraction to this channel is similar in the deuterated and non-deuterated systems and thus the larger than predicted branching to this channel may not be due to quantum tunneling. Rather, we consider how the branching to the water + vinyl channel might be sensitive to the angular momentum of the β -hydroxyethyl radicals.

References

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