

Unimolecular Dissociation of the CH_3OCO Radical: An Intermediate in the $\text{CH}_3\text{O} + \text{CO}$ Reaction

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This work investigates the unimolecular dissociation of the methoxycarbonyl, CH_3OCO , radical. Photolysis of methyl chloroformate at 193 nm produces nascent CH_3OCO radicals with a distribution of internal energies, determined by the velocities of the momentum-matched Cl atoms, that spans the theoretically predicted barriers to the $\text{CH}_3\text{O} + \text{CO}$ and $\text{CH}_3 + \text{CO}_2$ product channels. Both electronic ground- and excited-state radicals undergo competitive dissociation to both product channels. The experimental product branching to $\text{CH}_3 + \text{CO}_2$ from the ground-state radical, about 70%, is orders of magnitude larger than RRKM-predicted branching,

suggesting that previously calculated barriers to the $\text{CH}_3\text{OCO} \rightarrow \text{CH}_3 + \text{CO}_2$ reaction are dramatically in error. Our electronic structure calculations reveal that the cis conformer of the transition state leading to the $\text{CH}_3 + \text{CO}_2$ product channel has a much lower barrier than the trans transition state. RRKM calculations using this cis transition state give product branching in agreement with the experimental branching. The data also suggest that our experiments produce a low-lying excited state of the CH_3OCO radical and give an upper limit to its adiabatic excitation energy of 55 kcal/mole.