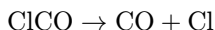


analysis the fraction is 15%, giving an average of 18%. Again, these values are within the range of uncertainty associated with the analysis.

These observations suggest a simple picture of the dissociation dynamics similar to that proposed for photodissociation of oxalyl chloride at 230 nm: the multiple bond-breaking processes for oxalyl chloride consists of two dissociation steps. The first step is an impulsive three-body dissociation,



which yields fast CO, Cl, and the chloroformyl radical ClCO. The measured distributions imply that little momentum is transferred to the ClCO in this step, with the impulse primarily along the C–Cl bond. In the second step, most of the remaining ClCO undergoes subsequent decomposition:



which yields slow CO and Cl. As suggested by the fast components of TOF spectra in Figs. 30 and 31, the fragments CO and Cl seem to be dynamically linked, that is, it is likely to break both the C–C and C–CCl bonds simultaneously. The direct observation of ClCO here confirms it as a primary product, and the translation energy distributions in Fig. 32 show clearly that there is no fast contribution in that product, consistent with the picture outlined above. The results confirm a previous study at 230 nm using the photofragment imaging technique, and provide a broad view of the overall dynamics of the process and details of the branching fractions unavailable to laser based studies. The use of this universal technique allows for complementary global insights into the dynamics when combined with the previous photofragment imaging study.

3.4. Propyne and Allene

A final illustration of the range of possibilities available for photochemistry studies using tunable VUV probe is provided by a recent study by Neumark and coworkers on the photodissociation of allene and propyne, two distinct C_3H_4 isomers.²⁷ In general for hydrocarbon photodissociation cleavage of the various inequivalent C–H bonds will result in chemically distinct isomers with the same mass, thereby complicating the identification of the primary photodissociation products. EI-based studies cannot distinguish among isomers except in unusual cases. Laser based methods such as laser induced fluorescence or REMPI can do better, but this requires a fuller