Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Unimolecular decomposition of formamide via direct chemical dynamics simulations

SUPPORTING INFORMATION

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Potential energy profiles

Potential energy profiles for decarbonylation, dehydrogenation, and dehydration from formamide are presented in Figures S1, S2, and S3, respectively. The stationary point energies and frequencies were computed using density functional B3LYP/aug-cc-pVDZ level of electronic structure theory.

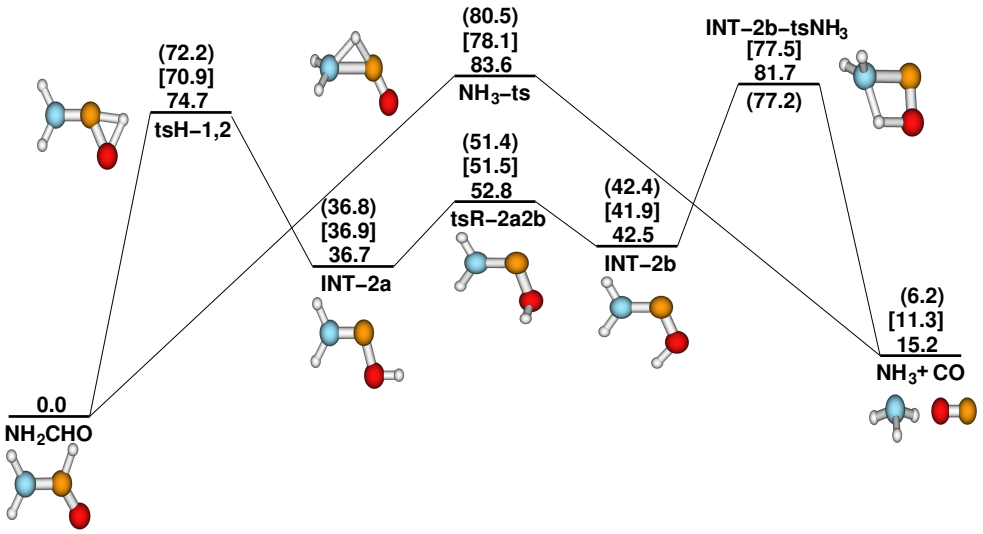

Figure S1: Potential energy profile for CO elimination pathways from formamide, computed using B3LYP/aug-cc-pVDZ theory. Numbers in square brackets are zero point corrected energy values and without brackets are zero point not corrected values. The numbers in parenthesis are benchmark CCSD(T)/CBS (zero point corrected) values taken from reference: Nguyen *et al.*, *J. Phys. Chem. A* 2011, **115**, 841 - 851.

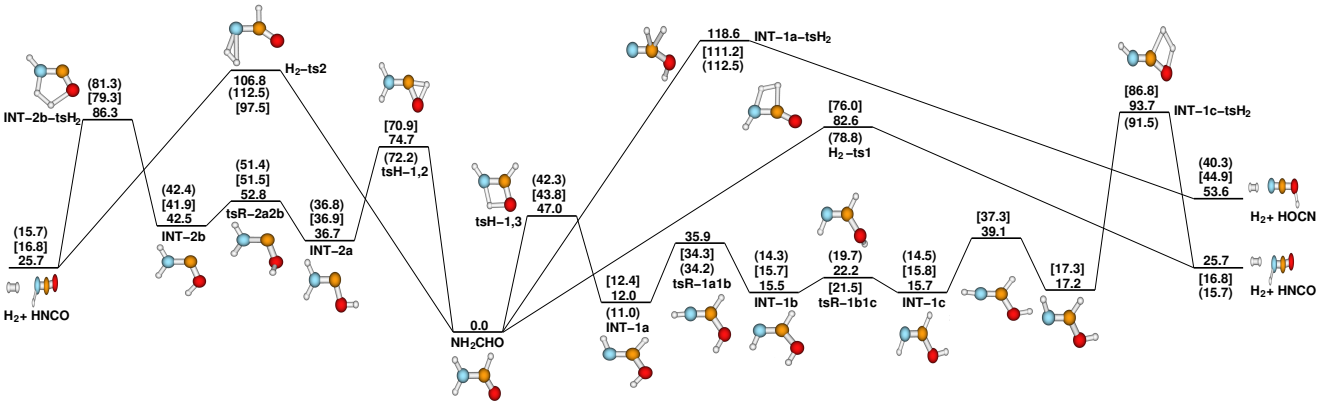

Figure S2: Potential energy profile for H_2 elimination pathways from formamide, computed using B3LYP/aug-cc-pVDZ theory. Numbers in square brackets are zero point corrected energy values and without brackets are zero point not corrected values. The numbers in parenthesis are benchmark CCSD(T)/CBS (zero point corrected) values taken from reference: Nguyen *et al.*, *J. Phys. Chem. A* 2011, **115**, 841 - 851.

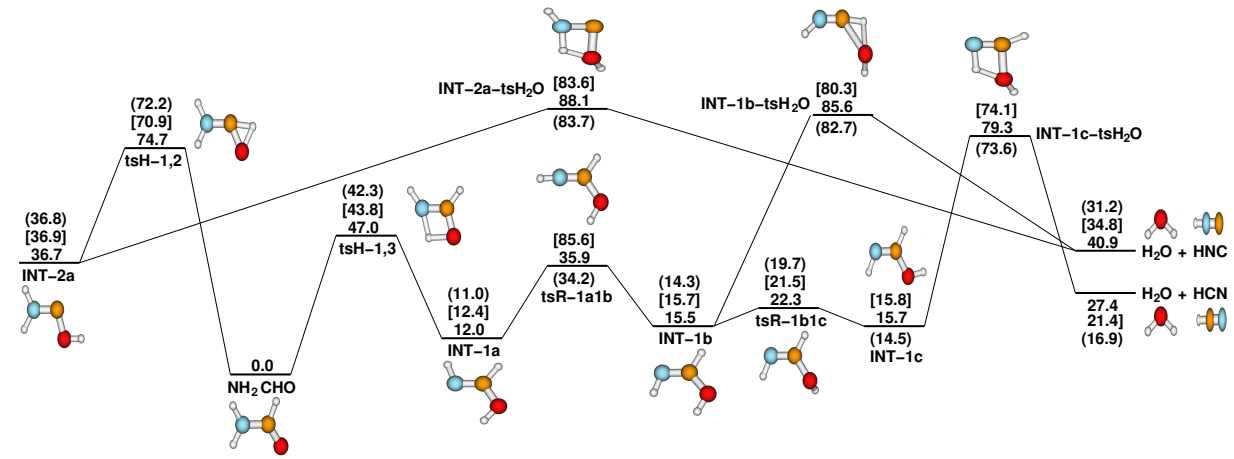

Figure S3: Potential energy profile for H_2O elimination pathways from formamide, computed using B3LYP/aug-cc-pVDZ theory. Numbers in square brackets are zero point corrected energy values and without brackets are zero point not corrected values. The numbers in parenthesis are benchmark CCSD(T)/CBS (zero point corrected) values taken from reference: Nguyen *et al.*, *J. Phys. Chem. A* 2011, **115**, 841 - 851.

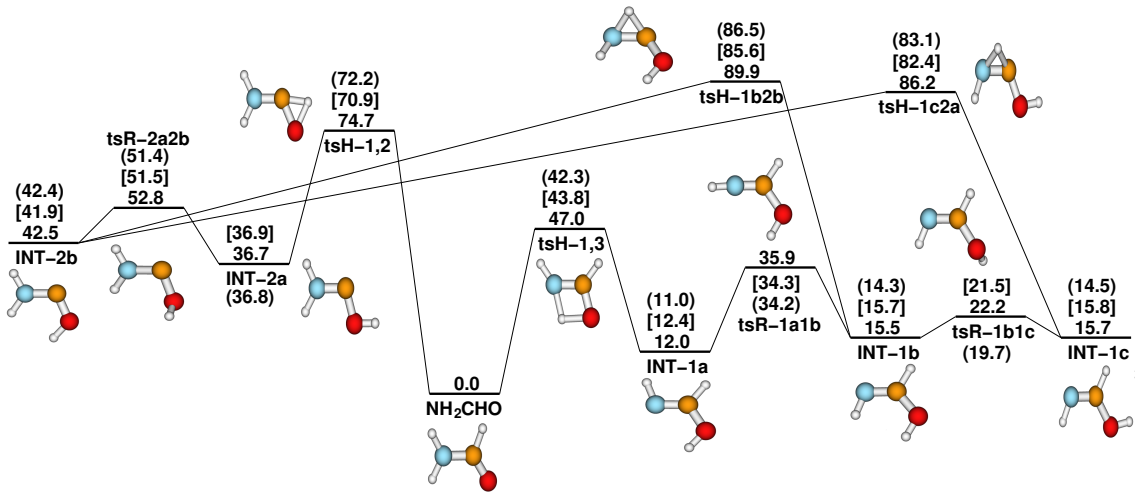

Figure S4: Potential energy profile for isomerization of formamide to aminohydroxycarbene (NH_2COH) and formimidic acid (NH=CH−OH), computed using B3LYP/aug-cc-pVDZ theory. Numbers in square brackets are zero point corrected energy values and without brackets are zero point not corrected values. The numbers in parenthesis are benchmark CCSD(T)/CBS (zero point corrected) values taken from reference: Nguyen *et al.*, *J. Phys. Chem. A* 2011, **115**, 841 - 851.

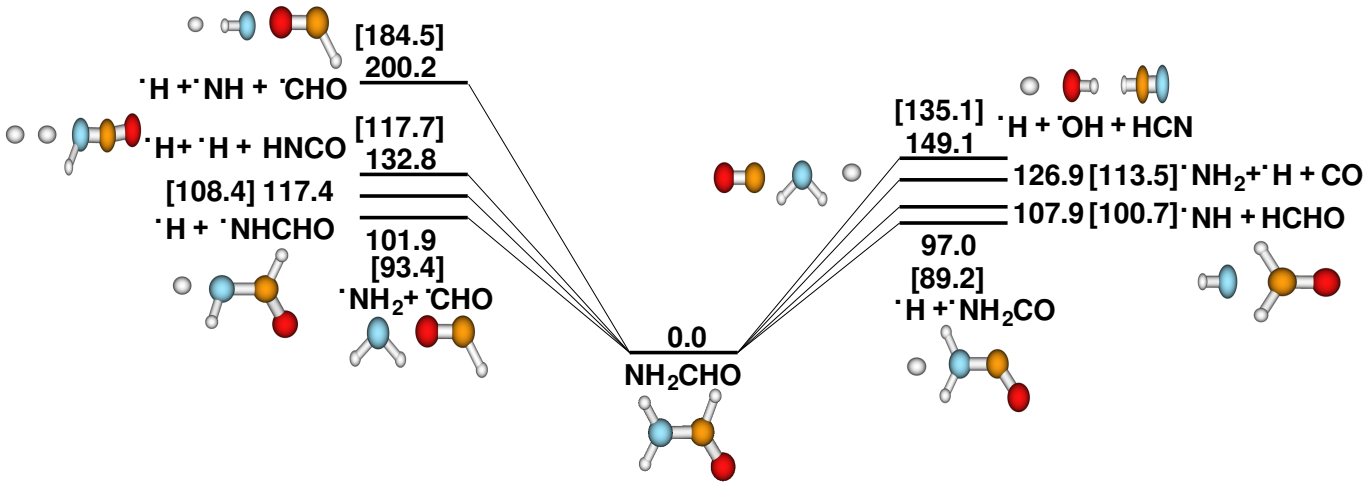

Figure S5: Potential energy profile for homolytic cleavages in formamide computed using B3LYP/aug-cc-pVDZ theory. The numbers in brackets are zero point corrected and numbers without brackets are zero point not corrected energy values computed using B3LYP/aug-cc-pVDZ theory

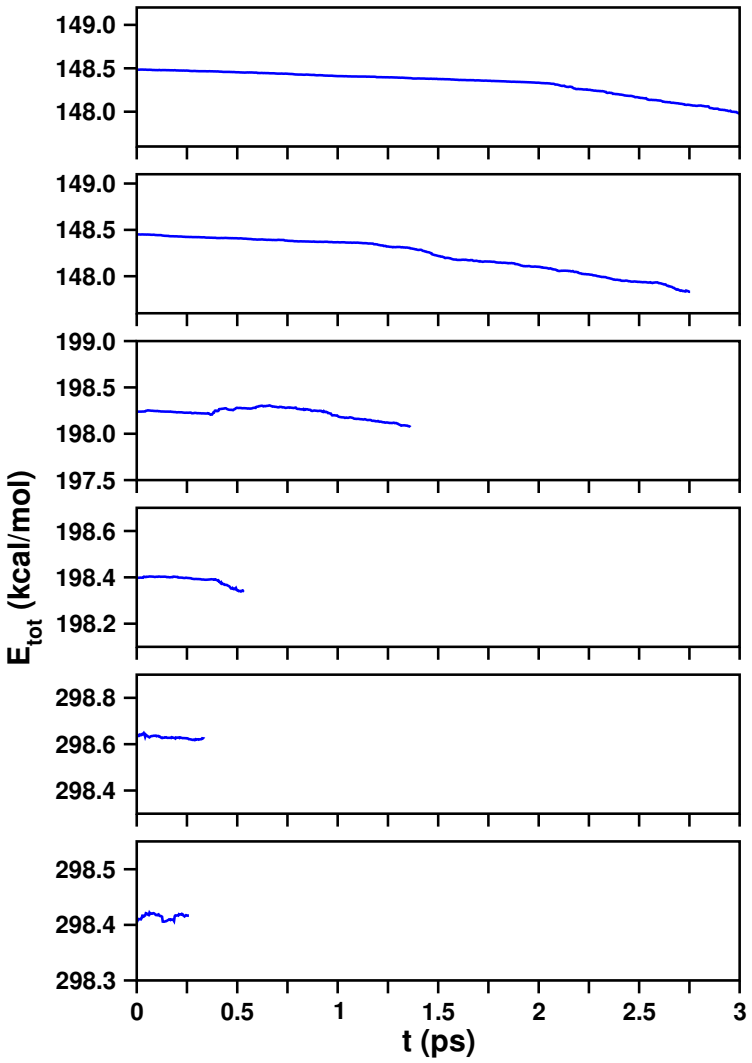

Figure S6: Total energy as a function of integration time for a few trajectories.

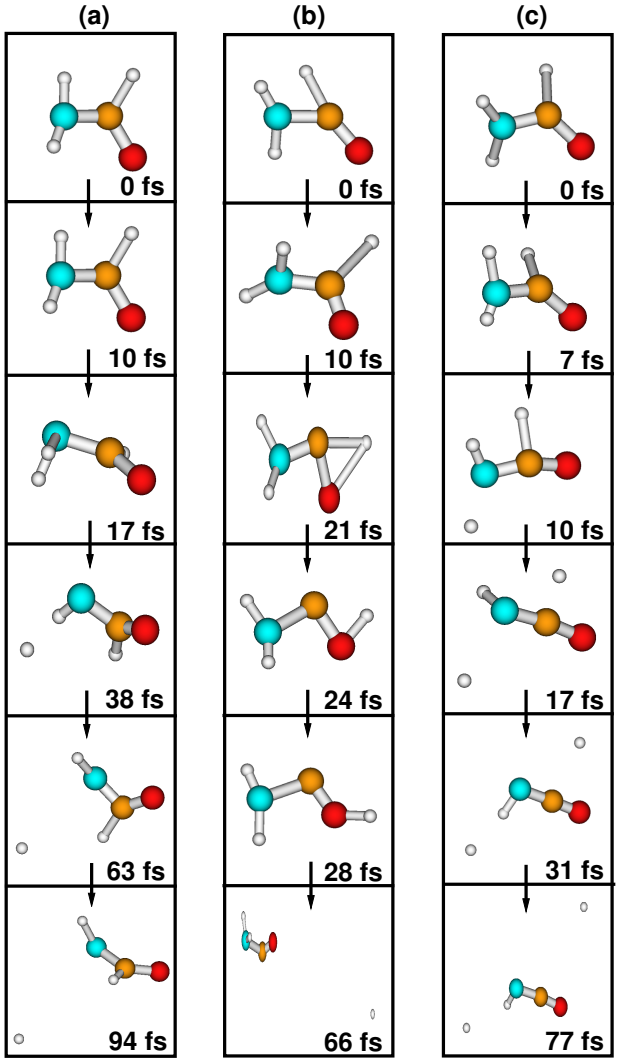

Figure S7: Snapshots of an example formamide decomposition trajectory showing (a) $NH_2CHO \longrightarrow H^{\cdot} + {}^{\cdot}NHCHO$ (b) $NH_2CHO \longrightarrow H^{\cdot} + NH_2{}^{\cdot}CO$ and (c) $NH_2CHO \longrightarrow HNCO + 2\,H^{\cdot}$.