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

Direct Dynamics in a Proton Transfer Reaction of Isomer Product Competition. Insight into the Suppressed Formation of Isoformyl cation

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Table S1. Electronic structure theory energies for stationary points on the $HOCO^+$ + CO PES with different methods[a,b] 修改

Species	MP2	M06	B3LYP	M06-2X	BhandH	PBE0	B97-1	CCSD(T)/CBS	CCSD[c]	Expt[d]
$CO_2\cdots HCO^+$	-131.0	-121.3	-119.2	-105.9	-130.1	-124.3	-119.7	-115.5		
	-125.1	-127.2	-115.1	-101.3	-125.5	-120.1	-115.5	-109.6	-102.1	
$CO_2\cdots HOC^+$	-43.5	-58.2	-53.1	-51.9	-70.3	-53.1	-52.3	-49.8		
	-39.7	-55.2	-50.2	-50.2	-68.2	-51.0	-49.8	-46.0	-40.6	
$[CO_2\cdot\cdot H\cdot\cdot CO]^+$	-11.3	-11.3	-10.0	-11.7	-18.4	-11.7	-12.1	-10.5		
	-9.6	-10.0	-8.8	-10.5	-16.7	-10.5	-10.9	-8.8	-5.0	
$HCO^+ + CO_2$	-69.5	-58.2	-52.3	-41.4	-45.2	-56.1	-51.9	-55.2		
	-65.7	-55.2	-48.5	-36.4	-41.4	-52.3	-48.5	-51.5	-44.4	-52.3
$HOC^+ + CO_2$	128.4	94.1	107.9	109.2	106.7	109.2	107.9	110.5		
	123.4	89.5	101.7	105.9	100.4	102.5	101.3	105.4	113.0	113.8

[a]Energies (in kJ mol^{-1}) are with respect to the $HOCO^+$ + CO reactants without (upper values) and with (lower numbers) ZPE. [b]MP2 and DFT energies are calculated with the aug-cc-pVDZ basis set and the CCSD(T)/CBS calculations based on the MP2 minimum geometries. [c]Energies from ref. 22 include ZPE at the CCSD/6-311++G(d,p) level. [d]Experimental data are from ref. 22,34.

Table S2. Averaged fractions of $HOCO^+ + CO \rightarrow HCO^+ + CO_2$ product energy partitioning[a]

	HCO^+		CO_2			
	f_{rot}'	f_{vib}'	f_{rot}'	f_{vib}'	f_{rel}'	f_{int}'
DR	0.22±0.04	0.19±0.03	0.18±0.03	0.09±0.02	0.32±0.04	0.68±0.04
DS	0.15±0.02	0.16±0.01	0.10±0.01	0.06±0.01	0.53±0.02	0.47±0.02
Ind	0.14±0.07	0.33±0.11	0.31±0.10	0.20±0.08	0.02±0.01	0.98±0.01
Total	0.16±0.01	0.17±0.01	0.12±0.01	0.07±0.01	0.48±0.02	0.52±0.02

[a]The *f*'s are fractions of energy partitioned to rotational, vibrational, relative translational, and internal (rotation + vibration) energy. Results are reported for the individual direct rebound (DR), direct stripping (DS), indirect (Ind) mechanisms, and for the total reaction.

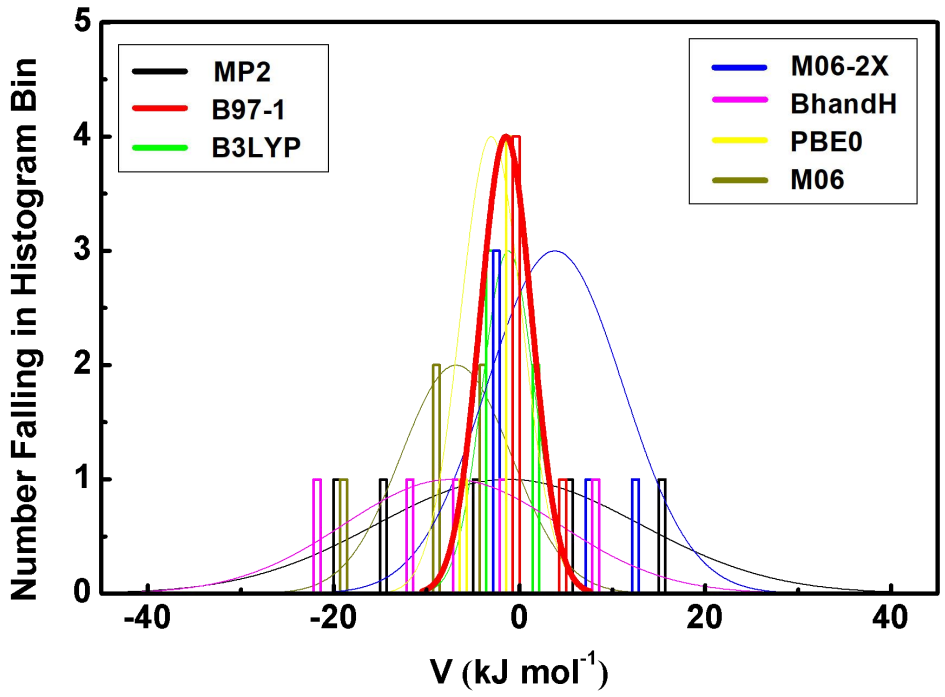

Figure S1. Histograms of differences between stationary point energies calculated with MP2 and DFT functionals, employing the aug-cc-pVDZ basis set, and the CCSD(T)/CBS values. All stationary point energies are included in each of the histograms and each is fit with the normal distribution of error curve with the fitting parameters given in the text.

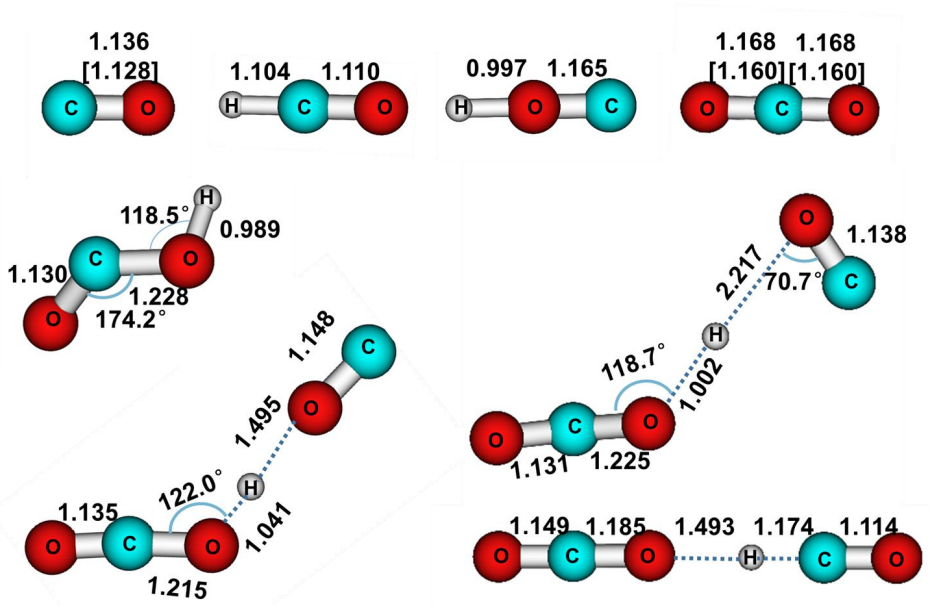

Figure S2. Stationary point structures for the $HOCO^+$ + CO reaction optimized at the B97-1/aug-cc-pVDZ level of theory. Bond distances (in Å) and angles (in degree) are shown for each structure and the available experimental data[a] are given in brackets. [a]Lide, D. R. CRC Handbook of Chemistry and Physics; CRC Press: Boca Raton, FL, 2005.

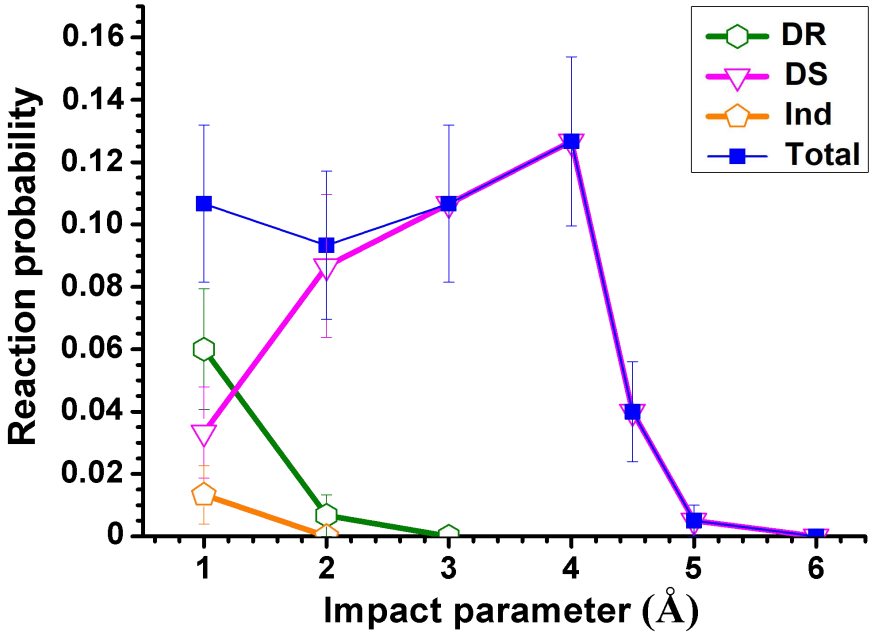

Figure S3. Reaction probability $P_r(b)$ of $HOCO^+ + CO \rightarrow HCO^+ + CO_2$ reaction channel as a function of impact parameter b at a 2.35eV collision energy. Results are shown for the three identified atomic-level reaction mechanisms and for the total reaction: direct rebound (green), direct stripping (pink), indirect (orange), and total (blue).

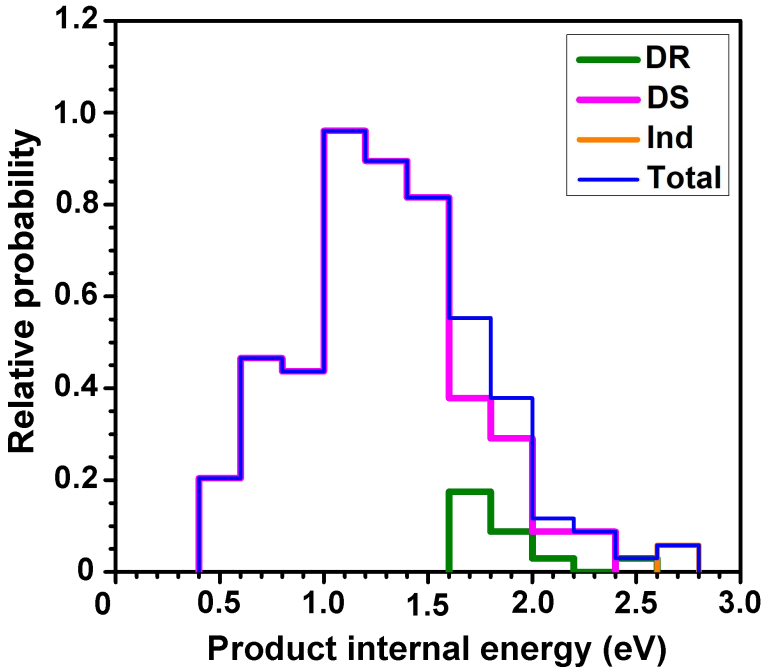

Figure S4. Product internal energy distributions of the proton transfer reaction $HOCO^+ + CO \rightarrow HCO^+ + CO_2$. Results are presented for the direct rebound (green), the direct stripping (pink), and the indirect (orange) atomic-level mechanisms, as well as for the total scattering (blue).

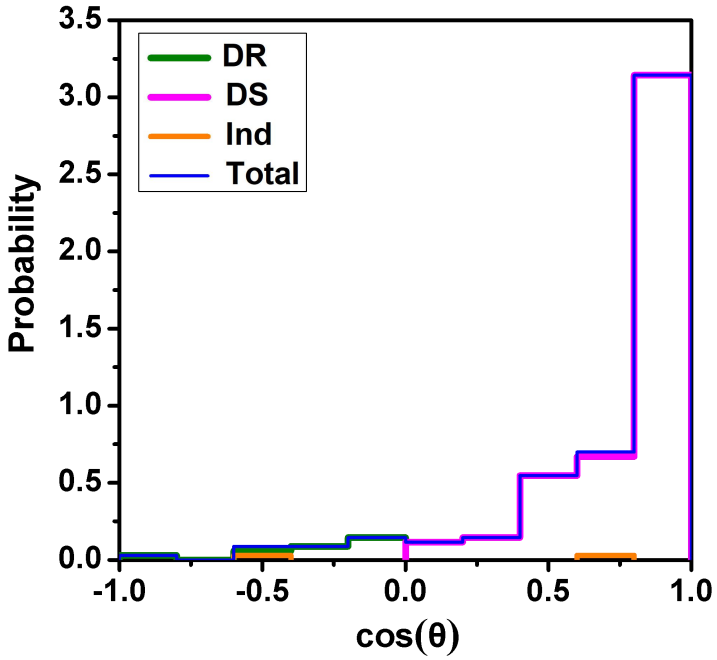

Figure S5. Velocity scattering angle distributions for the $HOCO^+ + CO \rightarrow HCO^+ + CO_2$ reaction. The results are illustrated for the individual direct rebound (green), direct stripping (pink), and indirect (orange) mechanisms and for the total scattering (blue).

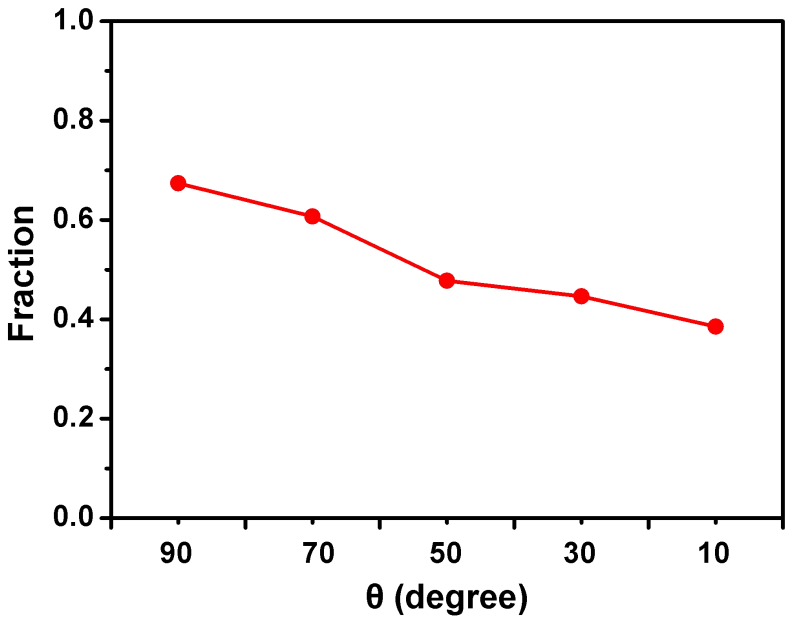

Figure S6. Fraction of product internal energy as a function of scattering angle for the $HOCO^+ + CO \rightarrow HCO^+ + CO_2$ reaction.