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

Reaction of Atomic Hydrogen with Formic Acid

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Supporting Information

Table S1. Optimized geometrical structures (in Å, for geometries, see Figure 1)

	UCCSD(T)/aug-cc-pVTZ			UMP2/aug-cc-pVTZ		
	***trans*-H_2COOH**					
O	0.642424	–1.161071	–0.442087	0.628612	–1.139207	–0.479227
O	–0.568332	0.821912	–0.147551	–0.555987	0.851213	–0.150258
C	0.506816	0.083415	0.195589	0.504880	0.085988	0.194461
H	0.429095	–0.026727	1.298197	0.411166	–0.047883	1.285197
H	–0.209726	–1.609314	–0.394611	–0.186265	–1.636426	–0.347492
H	1.431673	0.643366	–0.005566	1.429544	0.637896	0.001289
	***cis*-H_2COOH**					
O	0.596222	–1.219350	–0.370269	0.596183	–1.215859	–0.369153
O	–0.562915	0.739782	–0.174626	–0.561171	0.735334	–0.175478
C	0.518760	0.060865	0.222612	0.526240	0.062501	0.228402
H	0.477229	–0.007889	1.327891	0.473908	–0.006922	1.326285
H	1.389142	–1.658877	–0.044153	1.386666	–1.662157	–0.046663
H	1.404823	0.676870	–0.029634	1.401435	0.678503	–0.031572
	***cis-cis*-$HC(OH)_2$**					
O	–0.104223	–0.277994	–0.171228	–0.105525	–0.275694	–0.167506
C	0.011758	0.190317	1.110570	0.012188	0.191253	1.110635
H	0.868797	–0.177862	1.684958	0.866514	–0.176181	1.683347

O	–1.213048	0.081657	1.713750	–1.210179	0.082747	1.710290
H	–1.128977	0.418402	2.611232	–1.127653	0.414970	2.609911
H	0.756323	–0.193470	–0.593432	0.755269	–0.196057	–0.590817
	***trans-cis*-HC(OH)$_2$**					
O	–0.367634	–0.169133	–0.276201	0.103334	–0.128776	–0.163662
C	–0.248387	0.262465	1.033529	–0.002258	–0.177746	1.188906
H	0.738608	0.196728	1.488733	0.903550	0.170924	1.675030
O	–1.209720	–0.280663	1.830025	–1.197022	0.360247	1.625439
H	–2.028946	–0.302838	1.319861	–1.297002	0.146319	2.559295
H	0.211100	0.373440	–0.821967	–0.767329	–0.329928	–0.529148
	TS1					
O	-	-	-	–0.258742	–0.567366	–0.073026
C	-	-	-	–0.179602	0.172767	1.074632
H	-	-	-	0.780438	0.149278	1.586746
O	-	-	-	–1.276505	–0.049582	1.859215
H	-	-	-	–1.095085	0.307474	2.735709
H	-	-	-	–0.227231	0.028468	–0.827416
	TS2					
O	-	-	-	0.702922	–1.217024	–0.602230
O	-	-	-	–0.649680	0.604956	–0.038778

C	-	-	-	0.548632	–0.021606	0.014408
H	-	-	-	–0.170092	0.208249	1.023828
H	-	-	-	–0.183970	–1.581450	–0.733645
H	-	-	-	1.468397	0.557435	–0.001374

Table S2. Vibrational frequencies (in cm^{-1}) and intensities (in parentheses in km mol^{-1}) of *trans*-H_2COOH and *trans-cis*-$HC(OH)_2$ and their deuterated analogues obtained at the UMP2/aug-cc-pVTZ level of theory.

Unstable products				
No.	*trans*-H_2COOH	*trans*-H_2COOD	*trans*-HDCOOH (D4)[a]	*trans*-HDCOOH (D6)[b]
1	3832.4 (54.68)	3082.31 (3.42)	3832.72 (54.75)	3832.66 (54.97)
2	3081.6 (4.34)	2968.85 (25.21)	3077.35 (6.32)	2974.86 (22.84)
3	2968.6 (25.98)	2789.71 (35.58)	2174.05 (21.01)	2254.81 (7.26)
4	1432.3 (37.50)	1429.13 (28.63)	1401.40 (42.65)	1340.88 (5.08)
5	1398.3 (19.16)	1384.30 (10.21)	1265.42 (9.63)	1286.07 (87.73)
6	1335.4 (4.64)	1247.18 (197.41)	1243.41 (2.89)	1237.73 (20.50)
7	1140.9 (0.68)	1110.85 (178.44)	1108.26 (195.25)	1120.89 (123.04)
8	1108.9 (196.43)	1046.88 (7.14)	1018.67 (48.80)	1013.21 (31.57)
9	1016.7 (52.01)	926.77 (47.72)	908.88 (5.70)	915.15 (35.00)
10	795.67 (0.72)	773.84 (2.06)	683.45 (0.97)	697.20 (1.63)
11	556.00 (21.75)	537.21 (20.48)	553.02 (21.78)	550.10 (22.56)
12	272.74 (117.89)	205.83 (67.74)	271.17 (116.30)	271.99 (117.46)
Stable products				
No.	*trans-cis*-$HC(OH)_2$	*trans-cis*-HC(OD)(OH) *trans*-OD	*trans-cis*-HC(OH)(OD) *cis*-OD	*trans-cis*-$DC(OH)_2$
1	3845.4 (85.28)	3845.03 (82.07)	3811.92 (75.12)	3845.3 (85.29)
2	3811.2 (71.80)	3158.31 (28.93)	3157.88 (31.74)	3811.9 (72.87)

3	3157.3 (32.04)	2773.36 (47.75)	2799.07 (50.11)	2329.6 (27.16)
4	1419.8 (106.00)	1407.53 (71.54)	1414.56 (117.23)	1353.8 (42.09)
5	1366.1 (32.81)	1298.97 (54.28)	1328.50 (15.75)	1321.5 (215.63)
6	1210.5 (121.54)	1176.15 (267.03)	1203.87 (203.39)	1148.1 (191.46)
7	1149.8 (198.46)	1102.94 (38.27)	1099.98 (77.53)	1065.0 (34.94)
8	1071.2 (34.40)	1018.89 (0.60)	982.50 (40.86)	943.47 (11.88)
9	978.92 (33.63)	894.58 (46.91)	866.56 (32.41)	791.61 (17.69)
10	542.42 (20.51)	512.71 (19.42)	527.06 (20.28)	539.31 (21.05)
11	354.70 (172.90)	291.91 (168.38)	350.81 (140.67)	352.43 (174.16)
12	227.92 (68.44)	257.86 (21.79)	208.93 (44.44)	276.60 (66.57)

[a]D atom in position 4 (Figure 1). [b]D atom in position 6 (Figure 1).

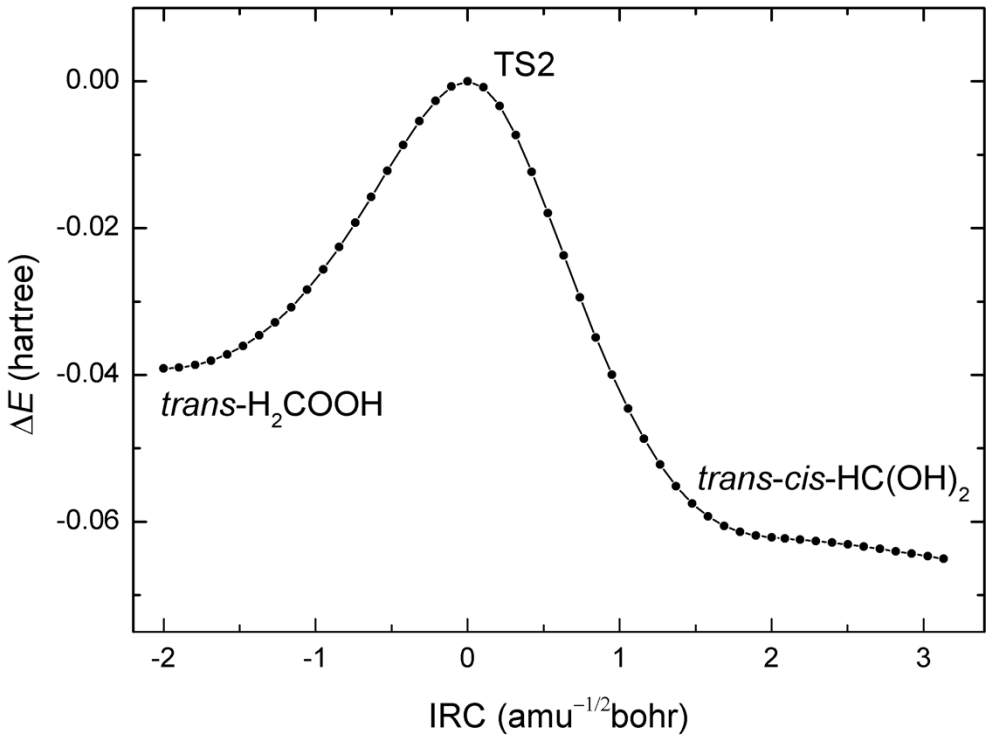

Figure S1. The change of the total energy for hydrogen atom transfer from *trans*-H_2COOH to *trans-cis*-$HC(OH)_2$ along the IRC path. The values of energy are calculated with respect to the transition state, for which the energy was set to zero.