Electronic Supplementary Material (ESI) for Chemical Science.

SUPPORTING INFORMATION

Aromatic Sulfonation with Sulfur Trioxide: Mechanism and Kinetic Model

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COMPUTATIONAL DETAILS

Metadynamics of benzene-S_2O_6 σ-complex in CH_3NO_2

An estimate of the additional free energy barrier required for sulfonation of the benzene-SO3 σ-complex with 1 assisting SO_3 in CH_3NO_2 is obtained with restrained MTD (rMTD), keeping the C-S_1 restrained to CN_{CS} = 0.5-0.6 with a harmonic potential. A single CV is defined as the coordination number CN_{CO}, which tracks the distance between the benzene C1 and the three O atoms of the assisting SO_3. Hill width = 0.02 and hill height = 0.2 kJ/mol. A set of twelve independent rMTD simulations is started from the benzene-SO_3 σ-complex + 1 assisting SO_3 and terminated as soon as the sulfonation reaction has taken place. From the set of 12 PMFs, an average PMF is calculated (Figure S1).

Low temperature MD of the σ-complex intermediate in CH_3NO_2

To verify if a metastable σ-complex intermediate state may exist, geometry optimization is performed of a snapshot located at TS from a MTD simulation in CH_3NO_2 solvent, followed by low-temperature MD (T = 1 K). A geometry similar to the previously optimized intermediate state[1] is formed, which remains stable for at least 40 ps (Figure S2).

1. G. Koleva, B. Galabov, J. Kong, H. F. Schaefer and P. v. R. Schleyer, *Journal of the American Chemical Society*, 2011, 133, 19094-19101.

Table S1. Mean geometric parameters at transition states and intermediate state.

participants				N[a]	r_{CS} (Å)	r_{CH} (Å)	r_{OH} (Å)	α_{CCH} (°)
2 SO_3	2D MTD	gas phase	TS	3	1.877	1.167	1.517	129
		CCl_3F	TS	3	1.853	1.114	1.604	118
		CH_3NO_2	TS	3	1.830	1.112	1.629	114
	rMD	gas phase	TS	2	1.862	1.197	1.510	118
		CCl_3F	TS	2	1.848	1.197	1.562	113
	1D rMTD	CH_3NO_2	TS	11	1.859	1.131	1.584	112
	MD (1K)	CH_3NO_2	I	15 ps[b]	1.957	1.121	1.934	129
2 SO_3 + 1 CH_3NO_2	1D rMTD	CH_3NO_2	TS1	1	1.847	1.098	1.731[c]	104
1 SO_3 +1 H_2SO_4	rMD	gas phase	TS1	1	1.893	1.131	1.656[d]	136
		CCl_3F	TS1	1	1.863	1.127	1.708[d]	106
		CH_3NO_2	TS2	1	1.869	1.095	1.621[d]	115

[a]number of geometries of which mean parameters are calculated.

[b]mean over over last 15 ps of a 40-ps simulation.

[c]minimal H_1-O distance between benzene and CH_3NO_2.

[d]minimal H_1-O distance between benzene and H_2SO_4.

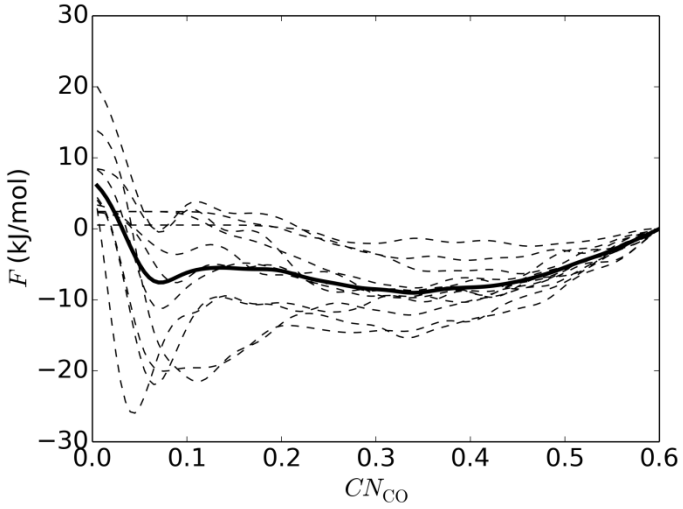
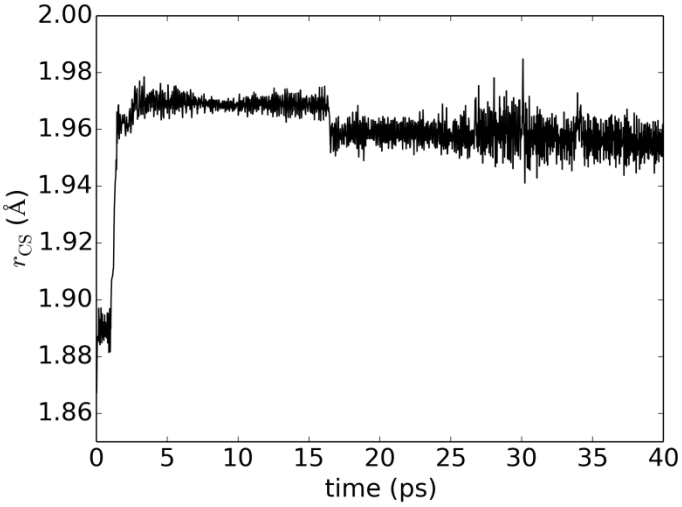
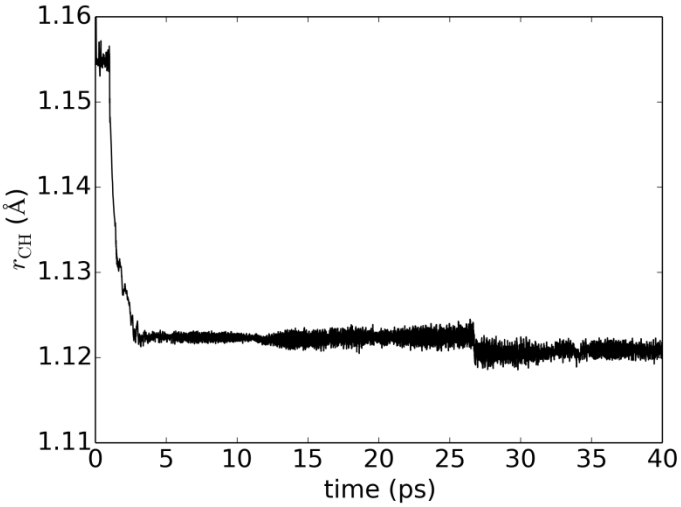


Figure S1. PMFs from twelve 1D rMTD simulations of the benzene-S_2O_6 σ-complex (dashed lines), and mean free energy profile (full line).


2.00
1.98
1.96
1.94
1.92
1.90
1.88
1.86
r_{CS} (Å)
0
5
10
15
20
25
30
35
40
time (ps)


1.16
1.15
1.14
1.13
1.12
1.11
r_{CH} (Å)
0
5
10
15
20
25
30
35
40
time (ps)

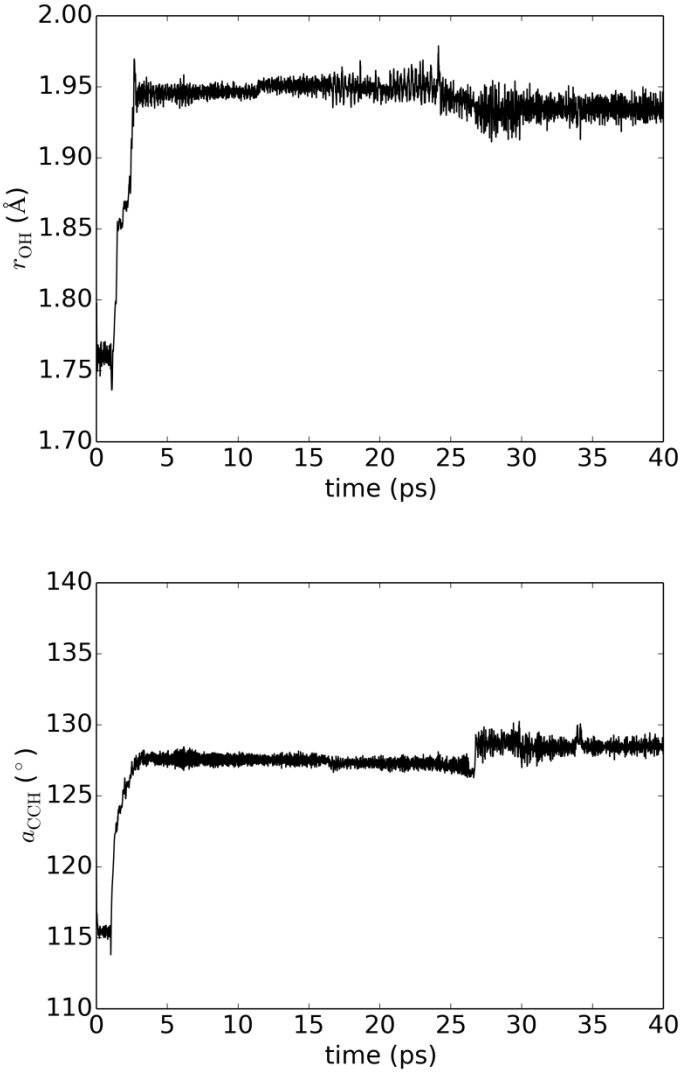


Figure S2. Evolution of geometric parameters of the benzene-S_2O_6 σ-complex intermediate state in CH_3NO_2 from an AIMD simulation at 1 K. From top to bottom: C_1-S_1 distance, C_1-H_1 distance, minimal O_2-H_1 distance, C_4-C_1-H_1 angle.