Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

Ambient Reaction Kinetics of Atmospheric Oxygenated Organics with the OH radical: A Computational Methodology Study

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T1-diagnostics

UCCSD(T)-F12a

Method	BH&HLYP	BMK	M06-2X	mPW1K	MP2
Methanol					
Pos-O	0.0355	**0.0607**	**0.0814**	**0.0493**	**0.0678**
Pos-α	0.0361	0.0255	0.0277	0.0318	0.0323
Ethanol					
Pos-O	**0.1084**	**0.0523**	**0.0668**	**0.1029**	**0.0570**
Pos-α	0.0321	0.0221	0.0247	0.0264	0.0288
Pos-β-OP	0.0237	0.0259	0.0248	0.0253	0.0247
Pos-β-IP	0.0236	0.0257	0.0242	0.0252	0.0246
Methanal					
Pos-α	**0.0452**	0.0212	0.0310	0.0321	**0.0433**
Ethanal					
Pos-α	0.0389	0.0210	0.0284	0.0242	0.0375
Pos-β	0.0308	0.0288	0.0269	0.0297	0.0292
Propanone					
Pos-α	0.0281	0.0265	0.0250	0.0273	0.0264
Dimethylether					
Pos-α	0.0343	0.0237	0.0260	0.0300	0.0308
Formic acid					
Pos-O	0.0299	**0.1554**	**0.1611**	0.0339	**0.0432**
Pos-α	0.0378	0.0327	0.0303	0.0357	0.0348
Acetic acid					
Pos-O	0.0256	**0.1483**	**0.1408**	0.0289	0.0384
Pos-α	0.0268	0.0259	0.0253	0.0260	0.0248
Methylformate					
Pos-acyl	0.0347	0.0291	0.0274	0.0325	0.0319
Pos-alkoxyl-OP	0.0270	0.0280	0.0266	0.0278	0.0271
Pos-alkoxyl-IP	0.0287	0.0276	0.0259	0.0285	0.0275

Table 1: The T1 diagnostric for the individual reaction channels calculated with UCCSD(T)-F12a/VTZ-F12

RCCSD(T)-F12a

Method	BH&HLYP	BMK	M06-2X	mPW1K	MP2
Methanol					
Pos-O	0.0287	**0.0454**	**0.0594**	0.0379	**0.0504**
Pos-α	0.0317	0.0228	0.0246	0.0282	0.0287
Ethanol					
Pos-O	**0.0665**	0.0392	**0.0490**	**0.0667**	**0.0427**
Pos-α	0.0283	0.0197	0.0222	0.0236	0.0256
Pos-β-OP	0.0217	0.0236	0.0227	0.0231	0.0227
Pos-β-IP	0.0216	0.0235	0.0219	0.0231	0.0226
Methanal					
Pos-α	0.0388	0.0196	0.0275	0.0283	0.0374
Ethanal					
Pos-α	0.0333	0.0193	0.0247	0.0217	0.0323
Pos-β	0.0275	0.0260	0.0246	0.0267	0.0264
Propanone					
Pos-α	0.0252	0.0240	0.0232	0.0246	0.0240
Dimethylether					
Pos-α	0.0299	0.0212	0.0231	0.0264	0.0271
Formic acid					
Pos-O	0.0227	**0.0665**	**0.0689**	0.0249	0.0381
Pos-α	0.0330	0.0290	0.0271	0.0314	0.0308
Acetic acid					
Pos-O	0.0195	**0.0606**	0.0325	0.0214	0.0340
Pos-α	0.0245	0.0240	0.0235	0.0240	0.0232
Methylformate					
Pos-acyl	0.0303	0.0259	0.0247	0.0286	0.0282
Pos-alkoxyl-OP	0.0247	0.0257	0.0246	0.0255	0.0251
Pos-alkoxyl-IP	0.0260	0.0252	0.0239	0.0259	0.0253

Table 2: The T1 diagnostic for the individual reaction channels calculated with RCCSD(T)-F12a/VTZ-F12

Unmodified rate constants

Method	BH&HLYP	BMK	M06-2X	mPW1K	CBS-QB3	G3	MP2	exp
Methanol	$5.6{\cdot}10^{-16}$	$2.3{\cdot}10^{-13}$	$8.1{\cdot}10^{-14}$	$1.5{\cdot}10^{-14}$	$2.3{\cdot}10^{-14}$	$3.3{\cdot}10^{-14}$	$3.0{\cdot}10^{-16}$	$9.0{\cdot}10^{-13} \pm 15\%$
Ethanol	$2.4{\cdot}10^{-15}$	$2.7{\cdot}10^{-13}$	$5.3{\cdot}10^{-13}$	$2.8{\cdot}10^{-14}$	$7.0{\cdot}10^{-14}$	$3.6{\cdot}10^{-13}$	$1.6{\cdot}10^{-15}$	$3.2{\cdot}10^{-12} \pm 10\%$
Methanal	$4.9{\cdot}10^{-14}$	$4.3{\cdot}10^{-13}$	$3.3{\cdot}10^{-12}$	$1.8{\cdot}10^{-14}$	$3.8{\cdot}10^{-13}$	$5.9{\cdot}10^{-12}$	$7.2{\cdot}10^{-16}$	$8.5{\cdot}10^{-12} \pm 15\%$
Ethanal	$3.4{\cdot}10^{-14}$	$2.7{\cdot}10^{-13}$	$6.3{\cdot}10^{-13}$	$2.4{\cdot}10^{-13}$	$3.1{\cdot}10^{-13}$	$1.3{\cdot}10^{-11}$	$4.4{\cdot}10^{-15}$	$1.5{\cdot}10^{-11} \pm 15\%$
Propanone	$1.2{\cdot}10^{-18}$	$2.9{\cdot}10^{-15}$	$1.0{\cdot}10^{-14}$	$1.4{\cdot}10^{-16}$	$8.1{\cdot}10^{-16}$	$9.8{\cdot}10^{-16}$	$7.2{\cdot}10^{-18}$	$1.8{\cdot}10^{-13} \pm 15\%$
Dimethylether	$1.2{\cdot}10^{-15}$	$8.4{\cdot}10^{-13}$	$2.1{\cdot}10^{-13}$	$2.3{\cdot}10^{-14}$	$6.7{\cdot}10^{-14}$	$2.0{\cdot}10^{-13}$	$8.0{\cdot}10^{-16}$	$2.7{\cdot}10^{-12} \pm 15\%$
Formic acid	$9.8{\cdot}10^{-19}$	$1.2{\cdot}10^{-14}$	$2.4{\cdot}10^{-15}$	$1.9{\cdot}10^{-16}$	$1.3{\cdot}10^{-16}$	$2.4{\cdot}10^{-16}$	$9.2{\cdot}10^{-19}$	$4.3{\cdot}10^{-13} \pm 30\%$
Acetic acid	$1.2{\cdot}10^{-19}$	$4.5{\cdot}10^{-16}$	$9.1{\cdot}10^{-16}$	$1.3{\cdot}10^{-17}$	$1.6{\cdot}10^{-16}$	$8.3{\cdot}10^{-17}$	$5.4{\cdot}10^{-18}$	$7.0{\cdot}10^{-13} \pm 20\%$
Methylformate	$4.4{\cdot}10^{-18}$	$2.6{\cdot}10^{-14}$	$4.0{\cdot}10^{-15}$	$5.7{\cdot}10^{-16}$	$3.9{\cdot}10^{-15}$	$1.1{\cdot}10^{-15}$	$2.0{\cdot}10^{-17}$	$1.8{\cdot}10^{-13} \pm 30\%$

Unmodified rate constants with Wigner tunnelling

Method	BH&HLYP	BMK	M06-2X	mPW1K	MP2	exp
Methanol	$3.8{\cdot}10^{-13}$	$1.2{\cdot}10^{-14}$	$3.0{\cdot}10^{-14}$	$2.5{\cdot}10^{-14}$	$1.3{\cdot}10^{-13}$	$9.0{\cdot}10^{-13} \pm 15\%$
Ethanol	$4.4{\cdot}10^{-15}$	$3.3{\cdot}10^{-13}$	$9.7{\cdot}10^{-13}$	$3.6{\cdot}10^{-14}$	$2.0{\cdot}10^{-14}$	$3.2{\cdot}10^{-12} \pm 10\%$
Methanal	$2.0{\cdot}10^{-12}$	$1.9{\cdot}10^{-14}$	$1.3{\cdot}10^{-12}$	$1.5{\cdot}10^{-13}$	$2.2{\cdot}10^{-15}$	$8.5{\cdot}10^{-12} \pm 15\%$
Ethanal	$4.1{\cdot}10^{-14}$	$2.8{\cdot}10^{-13}$	$7.3{\cdot}10^{-13}$	$2.4{\cdot}10^{-13}$	$8.4{\cdot}10^{-15}$	$1.5{\cdot}10^{-11} \pm 15\%$
Propanone	$4.6{\cdot}10^{-18}$	$5.2{\cdot}10^{-15}$	$3.3{\cdot}10^{-14}$	$3.5{\cdot}10^{-16}$	$2.6{\cdot}10^{-17}$	$1.8{\cdot}10^{-13} \pm 15\%$
Dimethylether	$2.7{\cdot}10^{-15}$	$9.4{\cdot}10^{-13}$	$3.3{\cdot}10^{-13}$	$2.8{\cdot}10^{-14}$	$2.1{\cdot}10^{-15}$	$2.7{\cdot}10^{-12} \pm 15\%$
Formic acid	$4.4{\cdot}10^{-18}$	$5.0{\cdot}10^{-14}$	$4.5{\cdot}10^{-15}$	$4.8{\cdot}10^{-16}$	$5.0{\cdot}10^{-18}$	$4.3{\cdot}10^{-13} \pm 30\%$
Acetic acid	$5.4{\cdot}10^{-19}$	$1.6{\cdot}10^{-15}$	$3.2{\cdot}10^{-15}$	$4.9{\cdot}10^{-17}$	$3.0{\cdot}10^{-17}$	$7.0{\cdot}10^{-13} \pm 20\%$
Methylformate	$1.9{\cdot}10^{-17}$	$4.7{\cdot}10^{-14}$	$9.4{\cdot}10^{-15}$	$1.4{\cdot}10^{-15}$	$9.3{\cdot}10^{-17}$	$1.8{\cdot}10^{-13} \pm 30\%$

Unmodified rate constants with Bell tunnelling

Method	BH&HLYP	BMK	M06-2X	mPW1K	MP2	exp
Methanol	$3.9{\cdot}10^{-12}$	$1.3{\cdot}10^{-14}$	$3.9{\cdot}10^{-14}$	$6.8{\cdot}10^{-14}$	$9.4{\cdot}10^{-12}$	$9.0{\cdot}10^{-13} \pm 15\%$
Ethanol	$5.7{\cdot}10^{-15}$	$4.3{\cdot}10^{-13}$	$1.0{\cdot}10^{-12}$	$5.6{\cdot}10^{-14}$	$5.9{\cdot}10^{-14}$	$3.2{\cdot}10^{-12} \pm 10\%$
Methanal	$2.6{\cdot}10^{-12}$	$1.9{\cdot}10^{-14}$	$1.4{\cdot}10^{-12}$	$1.5{\cdot}10^{-13}$	$1.8{\cdot}10^{-14}$	$8.5{\cdot}10^{-12} \pm 15\%$
Ethanal	$4.3{\cdot}10^{-14}$	$2.8{\cdot}10^{-13}$	$7.5{\cdot}10^{-13}$	$2.4{\cdot}10^{-13}$	$1.4{\cdot}10^{-14}$	$1.5{\cdot}10^{-11} \pm 15\%$
Propanone	$6.1{\cdot}10^{-16}$	$7.4{\cdot}10^{-15}$	$3.2{\cdot}10^{-13}$	$1.3{\cdot}10^{-15}$	$1.1{\cdot}10^{-15}$	$1.8{\cdot}10^{-13} \pm 15\%$
Dimethylether	$7.2{\cdot}10^{-15}$	$9.5{\cdot}10^{-13}$	$3.9{\cdot}10^{-13}$	$2.9{\cdot}10^{-14}$	$9.4{\cdot}10^{-15}$	$2.7{\cdot}10^{-12} \pm 15\%$
Formic acid	$6.0{\cdot}10^{-16}$	$9.1{\cdot}10^{-13}$	$3.1{\cdot}10^{-14}$	$1.3{\cdot}10^{-15}$	$1.7{\cdot}10^{-15}$	$4.3{\cdot}10^{-13} \pm 30\%$
Acetic acid	$2.2{\cdot}10^{-15}$	$3.3{\cdot}10^{-14}$	$1.2{\cdot}10^{-13}$	$7.5{\cdot}10^{-15}$	$5.3{\cdot}10^{-14}$	$7.0{\cdot}10^{-13} \pm 20\%$
Methylformate	$1.4{\cdot}10^{-15}$	$1.5{\cdot}10^{-13}$	$2.8{\cdot}10^{-14}$	$5.3{\cdot}10^{-15}$	$9.6{\cdot}10^{-15}$	$1.8{\cdot}10^{-13} \pm 30\%$

Unmodified rate constants with Eckart tunnelling

Method	BH&HLYP	BMK	M06-2X	mPW1K	MP2	exp
Methanol	$1.1{\cdot}10^{-12}$	$1.3{\cdot}10^{-14}$	$3.6{\cdot}10^{-14}$	$3.6{\cdot}10^{-14}$	$1.1{\cdot}10^{-12}$	$9.0{\cdot}10^{-13} \pm 15\%$
Ethanol	$3.8{\cdot}10^{-15}$	$3.6{\cdot}10^{-13}$	$9.4{\cdot}10^{-13}$	$3.8{\cdot}10^{-14}$	$1.1{\cdot}10^{-14}$	$3.2{\cdot}10^{-12} \pm 10\%$
Methanal	$2.4{\cdot}10^{-12}$	$1.9{\cdot}10^{-14}$	$1.4{\cdot}10^{-12}$	$1.5{\cdot}10^{-13}$	$7.0{\cdot}10^{-15}$	$8.5{\cdot}10^{-12} \pm 15\%$
Ethanal	$4.3{\cdot}10^{-14}$	$2.8{\cdot}10^{-13}$	$7.4{\cdot}10^{-13}$	$2.4{\cdot}10^{-13}$	$1.2{\cdot}10^{-14}$	$1.5{\cdot}10^{-11} \pm 15\%$
Propanone	$7.1{\cdot}10^{-17}$	$6.8{\cdot}10^{-15}$	$1.2{\cdot}10^{-13}$	$7.8{\cdot}10^{-16}$	$2.1{\cdot}10^{-16}$	$1.8{\cdot}10^{-13} \pm 15\%$
Dimethylether	$5.1{\cdot}10^{-15}$	$9.5{\cdot}10^{-13}$	$2.6{\cdot}10^{-13}$	$2.9{\cdot}10^{-14}$	$5.0{\cdot}10^{-15}$	$2.7{\cdot}10^{-12} \pm 15\%$
Formic acid	$8.0{\cdot}10^{-17}$	$3.1{\cdot}10^{-13}$	$9.4{\cdot}10^{-15}$	$8.6{\cdot}10^{-16}$	$1.9{\cdot}10^{-16}$	$4.3{\cdot}10^{-13} \pm 30\%$
Acetic acid	$4.3{\cdot}10^{-17}$	$8.9{\cdot}10^{-15}$	$2.2{\cdot}10^{-14}$	$6.5{\cdot}10^{-16}$	$1.3{\cdot}10^{-15}$	$7.0{\cdot}10^{-13} \pm 20\%$
Methylformate	$2.5{\cdot}10^{-16}$	$8.9{\cdot}10^{-14}$	$1.8{\cdot}10^{-14}$	$3.0{\cdot}10^{-15}$	$1.6{\cdot}10^{-15}$	$1.8{\cdot}10^{-13} \pm 30\%$

UCCSD(T)-F12a single point corrected rate constants

Method	BH&HLYP	BMK	M06-2X	mPW1K	MP2	exp
Methanol	$1.6{\cdot}10^{-13}$	$1.1{\cdot}10^{-14}$	$1.9{\cdot}10^{-14}$	$1.9{\cdot}10^{-14}$	$4.7{\cdot}10^{-14}$	$9.0{\cdot}10^{-13} \pm 15\%$
Ethanol	$5.2{\cdot}10^{-13}$	$3.2{\cdot}10^{-14}$	$1.5{\cdot}10^{-13}$	$5.5{\cdot}10^{-14}$	$2.4{\cdot}10^{-13}$	$3.2{\cdot}10^{-12} \pm 10\%$
Methanal	$6.1{\cdot}10^{-12}$	$6.1{\cdot}10^{-14}$	$9.9{\cdot}10^{-13}$	$1.3{\cdot}10^{-13}$	$4.6{\cdot}10^{-12}$	$8.5{\cdot}10^{-12} \pm 15\%$
Ethanal	$4.9{\cdot}10^{-12}$	$4.2{\cdot}10^{-14}$	$2.0{\cdot}10^{-13}$	$3.2{\cdot}10^{-13}$	$1.4{\cdot}10^{-11}$	$1.5{\cdot}10^{-11} \pm 15\%$
Propanone	$1.6{\cdot}10^{-15}$	$8.3{\cdot}10^{-16}$	$2.0{\cdot}10^{-15}$	$1.1{\cdot}10^{-15}$	$3.2{\cdot}10^{-16}$	$1.8{\cdot}10^{-13} \pm 15\%$
Dimethylether	$8.1{\cdot}10^{-13}$	$6.0{\cdot}10^{-14}$	$6.3{\cdot}10^{-14}$	$7.4{\cdot}10^{-14}$	$2.3{\cdot}10^{-13}$	$2.7{\cdot}10^{-12} \pm 15\%$
Formic Acid	$1.5{\cdot}10^{-15}$	$4.8{\cdot}10^{-16}$	$5.5{\cdot}10^{-16}$	$4.6{\cdot}10^{-16}$	$5.0{\cdot}10^{-16}$	$4.3{\cdot}10^{-13} \pm 30\%$
Acetic Acid	$1.9{\cdot}10^{-16}$	$2.0{\cdot}10^{-16}$	$2.2{\cdot}10^{-16}$	$1.8{\cdot}10^{-16}$	$1.2{\cdot}10^{-16}$	$7.0{\cdot}10^{-13} \pm 20\%$
Methyl Formate	$5.8{\cdot}10^{-15}$	$9.2{\cdot}10^{-16}$	$4.1{\cdot}10^{-16}$	$1.6{\cdot}10^{-15}$	$2.1{\cdot}10^{-15}$	$1.8{\cdot}10^{-13} \pm 30\%$

RCCSD(T)-F12a single point corrected rate constants

Method	BH&HLYP	BMK	M06-2X	mPW1K	MP2	exp
Methanol	$3.0{\cdot}10^{-14}$	$5.1{\cdot}10^{-15}$	$7.6{\cdot}10^{-15}$	$5.5{\cdot}10^{-15}$	$1.3{\cdot}10^{-14}$	$9.0{\cdot}10^{-13} \pm 15\%$
Ethanol	$1.1{\cdot}10^{-13}$	$1.6{\cdot}10^{-14}$	$6.0{\cdot}10^{-14}$	$1.9{\cdot}10^{-14}$	$6.6{\cdot}10^{-13}$	$3.2{\cdot}10^{-12} \pm 10\%$
Methanal	$6.8{\cdot}10^{-13}$	$4.3{\cdot}10^{-14}$	$3.7{\cdot}10^{-13}$	$4.5{\cdot}10^{-14}$	$5.8{\cdot}10^{-13}$	$8.5{\cdot}10^{-12} \pm 15\%$
Ethanal	$5.6{\cdot}10^{-13}$	$2.6{\cdot}10^{-14}$	$6.7{\cdot}10^{-14}$	$1.5{\cdot}10^{-13}$	$1.8{\cdot}10^{-12}$	$1.5{\cdot}10^{-11} \pm 15\%$
Propanone	$3.7{\cdot}10^{-16}$	$2.5{\cdot}10^{-16}$	$7.3{\cdot}10^{-16}$	$2.9{\cdot}10^{-16}$	$9.9{\cdot}10^{-17}$	$1.8{\cdot}10^{-13} \pm 15\%$
Dimethylether	$1.2{\cdot}10^{-13}$	$2.6{\cdot}10^{-14}$	$2.3{\cdot}10^{-14}$	$1.8{\cdot}10^{-14}$	$5.2{\cdot}10^{-14}$	$2.7{\cdot}10^{-12} \pm 15\%$
Formic Acid	$1.6{\cdot}10^{-16}$	$8.4{\cdot}10^{-17}$	$1.3{\cdot}10^{-16}$	$6.8{\cdot}10^{-17}$	$8.3{\cdot}10^{-17}$	$4.3{\cdot}10^{-13} \pm 30\%$
Acetic Acid	$5.4{\cdot}10^{-17}$	$1.0{\cdot}10^{-16}$	$5.0{\cdot}10^{-17}$	$5.8{\cdot}10^{-17}$	$4.4{\cdot}10^{-17}$	$7.0{\cdot}10^{-13} \pm 20\%$
Methyl Formate	$6.7{\cdot}10^{-16}$	$2.3{\cdot}10^{-16}$	$1.2{\cdot}10^{-16}$	$2.7{\cdot}10^{-16}$	$3.8{\cdot}10^{-16}$	$1.8{\cdot}10^{-13} \pm 30\%$

UCCSD(T)-F12a single point corrected rate constants with Wigner tunnelling

Method	BH&HLYP	BMK	M06-2X	mPW1K	MP2	exp
Methanol	$3.8{\cdot}10^{-13}$	$1.2{\cdot}10^{-14}$	$3.0{\cdot}10^{-14}$	$2.5{\cdot}10^{-14}$	$1.3{\cdot}10^{-13}$	$9.0{\cdot}10^{-13} \pm 15\%$
Ethanol	$9.1{\cdot}10^{-13}$	$3.7{\cdot}10^{-14}$	$2.2{\cdot}10^{-13}$	$6.7{\cdot}10^{-14}$	$4.9{\cdot}10^{-13}$	$3.2{\cdot}10^{-12} \pm 10\%$
Methanal	$1.0{\cdot}10^{-11}$	$6.1{\cdot}10^{-14}$	$1.4{\cdot}10^{-12}$	$1.4{\cdot}10^{-13}$	$1.4{\cdot}10^{-11}$	$8.5{\cdot}10^{-12} \pm 15\%$
Ethanal	$6.0{\cdot}10^{-12}$	$4.3{\cdot}10^{-14}$	$2.3{\cdot}10^{-13}$	$3.2{\cdot}10^{-13}$	$2.7{\cdot}10^{-11}$	$1.5{\cdot}10^{-11} \pm 15\%$
Propanone	$6.5{\cdot}10^{-15}$	$1.5{\cdot}10^{-15}$	$6.5{\cdot}10^{-15}$	$2.8{\cdot}10^{-15}$	$1.2{\cdot}10^{-15}$	$1.8{\cdot}10^{-13} \pm 15\%$
Dimethylether	$1.8{\cdot}10^{-12}$	$6.7{\cdot}10^{-14}$	$9.7{\cdot}10^{-14}$	$8.9{\cdot}10^{-14}$	$5.9{\cdot}10^{-13}$	$2.7{\cdot}10^{-12} \pm 15\%$
Formic acid	$6.8{\cdot}10^{-15}$	$1.8{\cdot}10^{-15}$	$1.1{\cdot}10^{-15}$	$1.2{\cdot}10^{-15}$	$2.7{\cdot}10^{-15}$	$4.3{\cdot}10^{-13} \pm 30\%$
Acetic acid	$9.0{\cdot}10^{-16}$	$7.1{\cdot}10^{-16}$	$7.8{\cdot}10^{-16}$	$6.9{\cdot}10^{-16}$	$6.6{\cdot}10^{-16}$	$7.0{\cdot}10^{-13} \pm 20\%$
Methylformate	$2.4{\cdot}10^{-14}$	$1.4{\cdot}10^{-15}$	$7.3{\cdot}10^{-16}$	$3.8{\cdot}10^{-15}$	$1.0{\cdot}10^{-14}$	$1.8{\cdot}10^{-13} \pm 30\%$

UCCSD(T)-F12a single point corrected rate constants with Bell tunnelling

Method	BH&HLYP	BMK	M06-2X	mPW1K	MP2	exp
Methanol	$1.1{\cdot}10^{-12}$	$1.6{\cdot}10^{-14}$	$3.9{\cdot}10^{-14}$	$6.3{\cdot}10^{-14}$	$7.2{\cdot}10^{-13}$	$9.0{\cdot}10^{-13} \pm 15\%$
Ethanol	$1.2{\cdot}10^{-12}$	$5.6{\cdot}10^{-14}$	$2.6{\cdot}10^{-13}$	$1.8{\cdot}10^{-13}$	$1.3{\cdot}10^{-12}$	$3.2{\cdot}10^{-12} \pm 10\%$
Methanal	$9.6{\cdot}10^{-12}$	$6.1{\cdot}10^{-14}$	$1.5{\cdot}10^{-12}$	$1.4{\cdot}10^{-13}$	$1.4{\cdot}10^{-11}$	$8.5{\cdot}10^{-12} \pm 15\%$
Ethanal	$6.2{\cdot}10^{-12}$	$4.3{\cdot}10^{-14}$	$2.3{\cdot}10^{-13}$	$3.3{\cdot}10^{-13}$	$2.6{\cdot}10^{-11}$	$1.5{\cdot}10^{-11} \pm 15\%$
Propanone	$1.2{\cdot}10^{-13}$	$2.1{\cdot}10^{-15}$	$6.1{\cdot}10^{-14}$	$9.9{\cdot}10^{-15}$	$2.2{\cdot}10^{-14}$	$1.8{\cdot}10^{-13} \pm 15\%$
Dimethylether	$3.5{\cdot}10^{-12}$	$6.8{\cdot}10^{-14}$	$1.2{\cdot}10^{-13}$	$9.1{\cdot}10^{-14}$	$1.6{\cdot}10^{-12}$	$2.7{\cdot}10^{-12} \pm 15\%$
Formic acid	$7.1{\cdot}10^{-14}$	$7.5{\cdot}10^{-14}$	$3.4{\cdot}10^{-15}$	$3.7{\cdot}10^{-15}$	$1.1{\cdot}10^{-13}$	$4.3{\cdot}10^{-13} \pm 30\%$
Acetic acid	$3.0{\cdot}10^{-14}$	$1.5{\cdot}10^{-14}$	$8.7{\cdot}10^{-15}$	$1.1{\cdot}10^{-14}$	$2.7{\cdot}10^{-14}$	$7.0{\cdot}10^{-13} \pm 20\%$
Methylformate	$2.1{\cdot}10^{-13}$	$2.2{\cdot}10^{-15}$	$1.4{\cdot}10^{-15}$	$1.1{\cdot}10^{-14}$	$1.9{\cdot}10^{-13}$	$1.8{\cdot}10^{-13} \pm 30\%$

UCCSD(T)-F12a single point corrected rate constants with Eckart tunnelling

Method	BH&HLYP	BMK	M06-2X	mPW1K	MP2	exp
Methanol	$6.8{\cdot}10^{-13}$	$1.3{\cdot}10^{-14}$	$3.6{\cdot}10^{-14}$	$3.5{\cdot}10^{-14}$	$3.4{\cdot}10^{-13}$	$9.0{\cdot}10^{-13} \pm 15\%$
Ethanol	$1.0{\cdot}10^{-12}$	$4.4{\cdot}10^{-14}$	$2.4{\cdot}10^{-13}$	$1.0{\cdot}10^{-13}$	$8.0{\cdot}10^{-13}$	$3.2{\cdot}10^{-12} \pm 10\%$
Methanal	$9.1{\cdot}10^{-12}$	$6.1{\cdot}10^{-14}$	$1.4{\cdot}10^{-12}$	$1.4{\cdot}10^{-13}$	$1.3{\cdot}10^{-11}$	$8.5{\cdot}10^{-12} \pm 15\%$
Ethanal	$6.0{\cdot}10^{-12}$	$4.2{\cdot}10^{-14}$	$2.3{\cdot}10^{-13}$	$3.2{\cdot}10^{-13}$	$2.4{\cdot}10^{-11}$	$1.5{\cdot}10^{-11} \pm 15\%$
Propanone	$3.9{\cdot}10^{-14}$	$1.9{\cdot}10^{-15}$	$2.4{\cdot}10^{-14}$	$5.9{\cdot}10^{-15}$	$6.2{\cdot}10^{-15}$	$1.8{\cdot}10^{-13} \pm 15\%$
Dimethylether	$2.6{\cdot}10^{-12}$	$6.8{\cdot}10^{-14}$	$1.1{\cdot}10^{-13}$	$9.1{\cdot}10^{-14}$	$1.1{\cdot}10^{-12}$	$2.7{\cdot}10^{-12} \pm 15\%$
Formic acid	$3.1{\cdot}10^{-14}$	$1.7{\cdot}10^{-14}$	$2.2{\cdot}10^{-15}$	$2.3{\cdot}10^{-15}$	$3.2{\cdot}10^{-14}$	$4.3{\cdot}10^{-13} \pm 30\%$
Acetic acid	$9.4{\cdot}10^{-15}$	$4.2{\cdot}10^{-15}$	$3.4{\cdot}10^{-15}$	$3.6{\cdot}10^{-15}$	$7.7{\cdot}10^{-15}$	$7.0{\cdot}10^{-13} \pm 20\%$
Methylformate	$9.7{\cdot}10^{-14}$	$1.9{\cdot}10^{-15}$	$1.1{\cdot}10^{-15}$	$7.0{\cdot}10^{-15}$	$6.7{\cdot}10^{-14}$	$1.8{\cdot}10^{-13} \pm 30\%$

Methanol UCCSD(T)-F12a absolute energies, ZPVE correction and partition functions

	E	ZPVE	Q
BH&HLYP			
TS CH	-191.2815	0.0597	7.11E+012
TS OH	-191.2765	0.0591	4.19E+012
Methanol	-115.6090	0.0530	2.88E+010
OH	-75.6740	0.0088	5.95E+007
RC	-191.2932	0.0646	-
PC CH	-191.3283	0.0633	-
PC OH	-191.3109	0.0631	-
BMK			
TS CH	-191.2811	0.0608	1.32E+013
TS OH	-191.2767	0.0585	3.55E+012
Methanol	-115.6092	0.0519	2.91E+010
OH	-75.6741	0.0086	6.05E+007
RC	-191.2935	0.0636	-
PC CH	-191.3285	0.0620	-
PC OH	-191.3111	0.0623	-
M06-2X			
TS CH	-191.2811	0.0596	7.86E+012
TS OH	-191.2770	0.0584	5.08E+012
Methanol	-115.6093	0.0518	2.84E+010
OH	-75.6741	0.0085	6.07E+007
RC	-191.2935	0.0632	-
PC CH	-191.3286	0.0623	-
PC OH	-191.3111	0.0616	-
mPW1K			
TS CH	-191.2805	0.0607	9.39E+012
TS OH	-191.2764	0.0590	4.33E+012
Methanol	-115.6090	0.0527	2.87E+010
OH	-75.6740	0.0088	5.95E+007
RC	-191.2932	0.0642	-
PC CH	-191.3283	0.0632	-
PC OH	-191.3109	0.0626	-
MP2			
TS CH	-191.2811	0.0589	8.26E+012
TS OH	-191.2767	0.0586	4.10E+012
Methanol	-115.6093	0.0519	3.03E+010
OH	-75.6741	0.0086	6.04E+007
RC	-191.2936	0.0633	-
PC CH	-191.3287	0.0620	-
PC OH	-191.3113	0.0621	-

Ethanol UCCSD(T)-F12a absolute energies, ZPVE correction and partition functions

	E	ZPVE	Q
BH&HLYP			
Pos O	-230.5387	0.0874	5.20E+013
Pos 1	-230.5459	0.0878	9.84E+013
Pos 2 OP	-230.5421	0.0879	2.49E+013
Pos 2 IP	-230.5379	0.0866	1.68E+014
Ethanol	-154.8712	0.0808	4.85E+011
OH	-75.6741	0.0086	6.04E+007
RC	-230.5559	0.0941	-
PC O	-230.5732	0.0919	-
PC 1	-230.5922	0.0927	-
PC 2 OP	-230.5774	0.0909	-
PC 2 IP	-230.5774	0.0909	-
BMK			
Pos O	-230.5391	0.0871	5.46E+013
Pos 1	-230.5455	0.0896	1.33E+014
Pos 2 OP	-230.5419	0.0872	2.77E+013
Pos 2 IP	-230.5376	0.0863	2.53E+014
Ethanol	-154.8715	0.0804	5.17E+011
OH	-75.6741	0.0086	6.05E+007
RC	-230.5563	0.0923	-
PC O	-230.5735	0.0905	-
PC 1	-230.5926	0.0903	-
PC 2 OP	-230.5778	0.0891	-
PC 2 IP	-230.5778	0.0891	-
M06-2X			
Pos O	-230.5395	0.0871	6.42E+013
Pos 1	-230.5454	0.0882	1.37E+014
Pos 2 OP	-230.5423	0.0877	2.45E+013
Pos 2 IP	-230.5379	0.0867	1.21E+014
Ethanol	-154.8716	0.0807	4.58E+011
OH	-75.6741	0.0085	6.07E+007
RC	-230.5544	0.0925	-
PC O	-230.5736	0.0901	-
PC 1	-230.5920	0.0913	-
PC 2 OP	-230.5779	0.0889	-
PC 2 IP	-230.5779	0.0889	-
mPW1K			
Pos O	-230.5385	0.0883	5.66E+013
Pos 1	-230.5448	0.0904	1.23E+014
Pos 2 OP	-230.5417	0.0887	3.13E+013
Pos 2 IP	-230.5374	0.0875	2.20E+014
Ethanol	-154.8712	0.0819	4.66E+011
OH	-75.6740	0.0088	5.95E+007
RC	-230.5560	0.0937	-
PC O	-230.5732	0.0913	-
PC 1	-230.5922	0.0923	-
PC 2 OP	-230.5775	0.0905	-
PC 2 IP	-230.5775	0.0905	-
MP2			
Pos O	-230.5391	0.0874	5.20E+013
Pos 1	-230.5456	0.0878	9.84E+013
Pos 2 OP	-230.5421	0.0879	2.49E+013
Pos 2 IP	-230.5377	0.0866	1.68E+014
Ethanol	-154.8716	0.0808	4.85E+011
OH	-75.6741	0.0086	6.04E+007
RC	-230.5565	0.0924	-
PC O	-230.5735	0.0915	-
PC 1	-230.5927	0.0909	-
PC 2 OP	-230.5780	0.0888	-
PC 2 IP	-230.5780	0.0888	-

Methanal UCCSD(T)-F12a absolute energies, ZPVE correction and partition functions

	E	ZPVE	Q
BH&HLYP			
TS CH	-190.0629	0.0347	3.85E+012
Methanal	-114.3873	0.0276	4.42E+009
OH	-75.6741	0.0088	5.95E+007
RC	-190.0694	0.0395	-
PC	-190.1151	0.0383	-
BMK			
TS CH	-190.0629	0.0372	4.15E+012
Methanal	-114.3877	0.0270	9.03E+009
OH	-75.6741	0.0086	6.05E+007
RC	-190.0698	0.0385	-
PC	-190.1155	0.0376	-
M06-2X			
TS CH	-190.0619	0.0349	1.90E+013
Methanal	-114.3878	0.0271	9.04E+009
OH	-75.6741	0.0085	6.07E+007
RC	-190.0694	0.0389	-
PC	-190.1156	0.0378	-
mPW1K			
TS CH	-190.0614	0.0365	7.08E+012
Methanal	-114.3874	0.0274	8.89E+009
OH	-75.6740	0.0088	5.95E+007
RC	-190.0695	0.0391	-
PC	-190.1133	0.0381	-
MP2			
TS CH	-190.0633	0.0342	6.03E+012
Methanal	-114.3879	0.0268	4.61E+009
OH	-75.6741	0.0086	6.04E+007
RC	-190.0694	0.0378	-
PC	-190.1156	0.0378	-

Ethanal UCCSD(T)-F12a absolute energies, ZPVE correction and partition functions

	E	ZPVE	Q
BH&HLYP			
BH&HLYP			
TS CH	-229.3357	0.0649	9.44E+013
TS CH3	-229.3256	0.0634	4.90E+013
Ethanal	-153.6582	0.0573	2.76E+011
OH	-75.6741	0.0088	5.95E+007
RC	-229.3420	0.0690	-
PC CH	-229.3849	0.0685	-
PC CH3	-229.3784	0.0689	-
BMK			
TS CH	-229.3349	0.0655	2.31E+013
TS CH3	-229.3253	0.0624	6.37E+013
Ethanal	-153.6586	0.0560	2.70E+011
OH	-75.6741	0.0086	6.05E+007
RC	-229.3427	0.0674	-
PC CH	-229.3856	0.0672	-
PC CH3	-229.3791	0.0674	-
M06-2X			
TS CH	-229.3342	0.0645	1.29E+014
TS CH3	-229.3256	0.0625	1.10E+014
Ethanal	-153.6587	0.0559	2.94E+011
OH	-75.6741	0.0085	6.07E+007
RC	-229.3427	0.0676	-
PC CH	-229.3857	0.0670	-
PC CH3	-229.3791	0.0678	-
mPW1K			
TS CH	-229.3339	0.0663	2.92E+014
TS CH3	-229.3251	0.0632	5.55E+013
Ethanal	-153.6583	0.0568	2.80E+011
OH	-75.6740	0.0088	5.95E+007
RC	-229.3421	0.0686	-
PC CH	-229.3853	0.0684	-
PC CH3	-229.3785	0.0684	-
MP2			
TS CH	-229.3361	0.0628	1.76E+014
TS CH3	-229.3254	0.0634	6.90E+013
Ethanal	-153.6588	0.0560	2.92E+011
OH	-75.6741	0.0086	6.04E+007
RC	-229.3426	0.0674	-
PC CH	-229.3858	0.0670	-
PC CH3	-229.3774	0.0682	-

Propanone UCCSD(T)-F12a absolute energies, ZPVE correction and partition functions

	E	ZPVE	Q
BH&HLYP			
TS CH	-268.5956	0.0923	8.17E+014
Methanal	-192.9268	0.0861	1.94E+013
OH	-75.6740	0.0088	5.95E+007
RC	-268.6120	0.0978	-
PC	-268.6472	0.0976	-
BMK			
TS CH	-268.5953	0.0904	3.68E+014
Methanal	-192.9273	0.0841	5.68E+012
OH	-75.6741	0.0086	6.05E+007
RC	-268.6126	0.0955	-
PC	-268.6478	0.0951	-
M06-2X			
TS CH	-268.5963	0.0906	3.52E+014
Methanal	-192.9275	0.0844	5.30E+012
OH	-75.6741	0.0085	6.07E+007
RC	-268.6121	0.0953	-
PC	-268.6479	0.0960	-
mPW1K			
TS CH	-268.5950	0.0919	9.37E+014
Methanal	-192.9269	0.0855	1.30E+013
OH	-75.6740	0.0088	5.95E+007
RC	-268.6119	0.0972	-
PC	-268.6473	0.0970	-
MP2			
TS CH	-268.5954	0.0912	1.04E+015
Methanal	-192.9275	0.0842	1.92E+013
OH	-75.6741	0.0086	6.04E+007
RC	-268.6128	0.0958	-
PC	-268.6460	0.0964	-

Dimethylether UCCSD(T)-F12a absolute energies, ZPVE correction and partition functions

	E	ZPVE	Q
BH&HLYP			
TS CH	-230.5254	0.0889	8.84E+013
Dimethylether	-154.8517	0.0822	4.71E+011
OH	-75.6740	0.0088	5.95E+007
RC	-230.5366	0.0940	-
PC	-230.5683	0.0924	-
BMK			
TS CH	-230.5250	0.0891	2.15E+014
Dimethylether	-154.8521	0.0802	5.38E+011
OH	-75.6741	0.0086	6.05E+007
RC	-230.5369	0.0925	-
PC	-230.5687	0.0912	-
M06-2X			
TS CH	-230.5249	0.0883	7.76E+013
Dimethylether	-154.8523	0.0806	4.38E+011
OH	-75.6741	0.0085	6.07E+007
RC	-230.5370	0.0919	-
PC	-230.5689	0.0911	-
mPW1K			
TS CH	-230.5243	0.0897	1.11E+014
Dimethylether	-154.8518	0.0816	4.73E+011
OH	-75.6740	0.0088	5.95E+007
RC	-230.5366	0.0933	-
PC	-230.5683	0.0919	-
MP2			
TS CH	-230.5252	0.0876	9.10E+013
Dimethylether	-154.8523	0.0808	4.70E+011
OH	-75.6741	0.0086	6.04E+007
RC	-230.5371	0.0923	-
PC	-230.5690	0.0906	-

Formic acid UCCSD(T)-F12a absolute energies, ZPVE correction and partition functions

	E	ZPVE	Q
BH&HLYP			
TS O	-265.2575	0.0407	5.66E+012
TS CH	-265.2608	0.0408	2.62E+013
Formic acid	-189.5926	0.0352	1.14E+011
OH	-75.6740	0.0088	5.95E+007
RC	-265.2748	0.0467	-
PC O	-265.2801	0.0452	-
PC CH	-265.3124	0.0475	-
BMK			
TS O	-265.2598	0.0397	5.67E+012
TS CH	-265.2601	0.0407	5.99E+013
Formic acid	-189.5931	0.0345	1.16E+011
OH	-75.6741	0.0086	6.05E+007
RC	-265.2788	0.0464	-
PC O	-265.2821	0.0422	-
PC CH	-265.3130	0.0461	-
M06-2X			
TS O	-265.2602	0.0396	5.77E+012
TS CH	-265.2605	0.0404	5.00E+013
Formic acid	-189.5933	0.0343	1.17E+011
OH	-75.6741	0.0085	6.07E+007
RC	-265.2753	0.0463	-
PC O	-265.2790	0.0451	-
PC CH	-265.3131	0.0464	-
mPW1K			
TS O	-265.2578	0.0409	5.26E+012
TS CH	-265.2598	0.0409	2.96E+013
Formic acid	-189.5927	0.0350	1.14E+011
OH	-75.6740	0.0088	5.95E+007
RC	-265.2719	0.0458	-
PC O	-265.2802	0.0444	-
PC CH	-265.3125	0.0475	-
MP2			
TS O	-265.2622	0.0439	2.47E+012
TS CH	-265.2604	0.0394	3.45E+013
Formic acid	-189.5933	0.0339	1.20E+011
OH	-75.6741	0.0086	6.04E+007
RC	-265.2773	0.0455	-
PC O	-265.2808	0.0438	-
PC CH	-265.3133	0.0459	-

Acetic acid UCCSD(T)-F12a absolute energies, ZPVE correction and partition functions

	E	ZPVE	Q
BH&HLYP			
Pos O	-304.5263	0.0692	1.75E+014
Pos 1	-304.5278	0.0700	3.56E+014
Acetic acid	-228.8616	0.0639	2.87E+012
OH	-75.6740	0.0088	5.95E+007
RC	-304.5445	0.0759	-
PC O	-304.5500	0.0738	-
PC CH	-304.5834	0.0761	-
BMK			
Pos O	-304.5291	0.0683	5.71E+013
Pos 1	-304.5286	0.0689	2.25E+014
Acetic acid	-228.8622	0.0626	1.62E+012
OH	-75.6741	0.0086	6.05E+007
RC	-304.5477	0.0745	-
PC O	-304.5552	0.0732	-
PC CH	-304.5841	0.0749	-
M06-2X			
Pos O	-304.5294	0.0678	8.08E+013
Pos 1	-304.5288	0.0687	2.16E+014
Acetic acid	-228.8624	0.0626	1.93E+012
OH	-75.6741	0.0085	6.07E+007
RC	-304.5450	0.0739	-
PC O	-304.5496	0.0730	-
PC CH	-304.5842	0.0739	-
mPW1K			
Pos O	-304.5266	0.0693	1.99E+014
Pos 1	-304.5279	0.0700	4.62E+014
Acetic acid	-228.8617	0.0635	2.87E+012
OH	-75.6740	0.0088	5.95E+007
RC	-304.5440	0.0755	-
PC O	-304.5502	0.0733	-
PC CH	-304.5835	0.0759	-
MP2			
Pos O	-304.5323	0.0720	6.74E+013
Pos 1	-304.5287	0.0686	3.45E+014
Acetic acid	-228.8624	0.0622	2.94E+012
OH	-75.6741	0.0086	6.04E+007
RC	-304.5448	0.0740	-
PC O	-304.5506	0.0721	-
PC CH	-304.5841	0.0743	-

Methyl Formate UCCSD(T)-F12a absolute energies, ZPVE correction and partition functions

	E	ZPVE	Q
BH&HLYP			
Acyl	-304.5043	0.0699	3.56E+014
Alkoxyl IP	-304.5012	0.0701	3.46E+014
Alkoxyl OP	-304.5056	0.0708	8.41E+013
Methyl formate	-228.8347	0.0643	1.91E+012
OH	-75.6740	0.0088	5.95E+007
RC	-304.5184	0.0759	-
PC - Acyl	-304.5458	0.0753	-
PC - Alkoxyl	-304.5454	0.0734	-
BMK			
Acyl	-304.5037	0.0698	3.14E+014
Alkoxyl IP	-304.5009	0.0691	6.91E+014
Alkoxyl OP	-304.5055	0.0699	6.45E+013
Methyl formate	-228.8353	0.0633	1.34E+012
OH	-75.6741	0.0086	6.05E+007
RC	-304.5184	0.0759	-
PC - Acyl	-304.5483	0.0754	-
PC - Alkoxyl	-304.5459	0.0727	-
M06-2X			
Acyl	-304.5042	0.0694	3.53E+014
Alkoxyl IP	-304.5014	0.0693	4.64E+014
Alkoxyl OP	-304.5060	0.0699	6.18E+013
Methyl formate	-228.8356	0.0626	2.61E+012
OH	-75.6741	0.0085	6.07E+007
RC	-304.5192	0.0748	-
PC - Acyl	-304.5486	0.0746	-
PC - Alkoxyl	-304.5463	0.0724	-
mPW1K			
Acyl	-304.5034	0.0698	3.98E+014
Alkoxyl IP	-304.5005	0.0700	3.71E+014
Alkoxyl OP	-304.5051	0.0706	8.04E+013
Methyl formate	-228.8348	0.0639	1.91E+012
OH	-75.6740	0.0088	5.95E+007
RC	-304.5185	0.0754	-
PC - Acyl	-304.5476	0.0752	-
PC - Alkoxyl	-304.5455	0.0731	-
MP2			
Acyl	-304.5042	0.0683	4.27E+014
Alkoxyl IP	-304.5013	0.0685	5.67E+014
Alkoxyl OP	-304.5058	0.0694	7.09E+013
Methyl formate	-228.8356	0.0627	1.86E+012
OH	-75.6741	0.0086	6.04E+007
RC	-304.5192	0.0739	-
PC - Acyl	-304.5488	0.0738	-
PC - Alkoxyl	-304.5464	0.0718	-