SUPPLEMENTARY INFORMATION

Data related to measured and estimated temperature-dependent, $k(T)$, and room-temperature, k_{298}, kinetics of the set of ethers and haloethers considered in this work are detailed in SI-1, SI-5 and the *SI_k298_kT_values.xlsx* excel file. Additional plots that extend Figure 4 and Figure 8 are provided for different complexes in SI-2 and SI-6 respectively. Intercomparison between the $k(T)$ estimated by each method are presented in SI-7. Detailed calculations for the rate coefficient and effective tunnelling parameter are provided to give more insight to the reader on how the method and the code work (SI-3, SI-4, and the *SI_calculations.xlsx* file). The main programme is provided in Python, with details in the SI-8 and the *READ_ME.txt* file.

SI-1: Values of k_{298} (experimental and predicted) and Arrhenius parameters (experimental) tabulated from the dataset studied.

See Excel file "**SI_k298_kT_values.xlsx**".

Table SI-1: Experimental and predicted room-temperature rate coefficients (k_{298}) for the studied dataset, in cm³ molecule^{-1} s^{-1}. Experimental data include Arrhenius parameters (A_{exp}, in cm³ molecule^{-1} s^{-1}, $(E_a/R)_{exp}$, in K, and n_{exp}) and the corresponding temperature ranges (from T_{low} to T_{high} in K). Predicted rate coefficients using the E-stateXvdW method from this work are reported at room-temperature, in cm³ molecule^{-1} s^{-1}. The excel spreadsheet contains the additional predicted data using EPI Suite/Kwok and Atkinson (1995), Jenkin et al. (2018) and Carter (2021).[1–4]

	Name	SMILES	Ref.	k_{exp}(298K)	A_{exp}	$(E_a/R)_{exp}$	n_{exp}	T_{low}	T_{high}	$k_{E\text{-}stateXvdW}$(298K)
1	methoxymethane	COC	*a*	2,76E-12	7,97E-13	-373,98	2,26	195.0	1470.0	1,32E-12
2	methoxyethane	COCC	*a*	6,56E-12	1,70E-13	-1095	3,26	276.0	753.0	4,89E-12
3	dimethoxymethane	COCOC	*a*	4,54E-12	2,70E-14	-1532	4,62	231.0	617.0	5,09E-12
4	2,4,6,8-Tetraoxanonane	COCOCOCOC	*b*	1E-11						8,49E-12
5	2,4,6,8,10-Pentaoxaundecane	COCOCOCOCOC	*b*	1,1E-11						9,94E-12
6	1,3-dimethoxypropane	COCCCOC	*a*	4,93E-11						1,67E-11
7	1,2-dimethoxyethane	COCCOC	*a*	2,8E-11	4,77E-13	-1220	2	234.0	372.0	1,25E-11
8	1-methoxypropane	CCCOC	*a*	9,91E-12						1,05E-11
9	1-propoxypropane	CCCOCCC	*a*	2,09E-11	1,21E-12	-854	2,19	230.0	1381.0	2,14E-11
10	di-n-propoxymethane	CCCOCOCCC	*a*	2,7E-11	4,30E-12	-546		263.0	400.0	3,80E-11
11	di-n-pentyl ether	CCCCCOCCCCC	*a*	3,3E-11	7,80E-12	-429		263.0	373.0	3,01E-11
12	1-methoxybutane	CCCCOC	*a*	1,45E-11	1,01E-11	-107		247.0	353.0	1,27E-11
13	1-ethoxybutane	CCCCOCC	*a*	2,2E-11	6,60E-12	-362		243.0	371.0	1,74E-11
14	di-n-butyl ether	CCCCOCCCC	*a*	2,75E-11	9,50E-14	-1697	3,82	230.0	1288.0	2,64E-11
15	di-n-butoxymethane	CCCCOCOCCCC	*a*	3,6E-11	5,20E-12	-580		260.0	400.0	4,46E-11
16	2-ethoxy-2-methylpropane	CCOC(C)(C)C	*a*	8,7E-12	3,40E-12	-280		230.0	400.0	8,70E-12
17	ethoxyethane	CCOCC	*a*	1,25E-11	4,21E-13	-1014,86	2,67	230.0	1351.0	9,04E-12
18	ethyl propyl ether	CCOCCC	*a*	1,12E-11						1,51E-11
19	1-ethoxy-2-methoxyethane	CCOCCOC	*a*	1,75E-11						1,88E-11
20	1,2-diethoxyethane	CCOCCOCC	*a*	5,7E-11	5,22E-13	-1400	2	298.0	372.0	2,74E-11
21	diethoxymethane	CCOCOCC	*a*	1,97E-11	3,42E-13	-1212	2	252.0	400.0	1,79E-11
22	trimethoxymethane	COC(OC)OC	*a*	5E-12	4,40E-14	-1408,3	4,45	298.0	744.0	3,35E-12
23	methyl t-butyl ether	CC(C)(C)OC	*a*	3,1E-12	1,87E-13	-843	3,34	231.0	753.0	4,54E-12
24	di-tert-butyl ether	CC(C)(C)OC(C)(C)C	*a*	3,7E-12						9,11E-12
25	dimethoxypropane	CC(C)(OC)OC	*a*	4,1E-12	3,73E-12	-30		240.0	440.0	5,63E-12
26	2,2-diethoxypropane	CC(C)(OCC)OCC	*a*	1,11E-11	1,06E-11	-15		240.0	440.0	1,85E-11
27	di-isobutoxymethane	CC(C)COCOCC(C)C	*a*	3,6E-11						2,72E-11
28	diisopropyl ether	CC(C)OC(C)C	*a*	1E-11	2,97E-12	-361		230.0	400.0	6,73E-12
29	di-isopropoxymethane	CC(C)OCOC(C)C	*a*	3,8E-11	4,40E-12	-646		250.0	400.0	1,42E-11
30	1,2-dimethoxypropane	CC(COC)OC	*c*	1,43E-11						1,07E-11
31	di-isobutyl ether	CC(COCC(C)C)C	*a*	2,6E-11						1,51E-11
32	1,1-dimethoxyethane	CC(OC)OC	*a*	8,9E-12						4,57E-12

33	isopropyl isobutyl ether	CC(OCC(C)C)C	*a*	2,1E-11						1,09E-11
34	methyl s-butyl ether	CCC(C)OC	*a*	9,67E-12						8,93E-12
35	di-2-butoxymethane	CCC(C)OCOC(C)CC	*a*	4,3E-11	8,70E-12	-477		260.0	401.0	3,28E-11
36	2-methoxy-2-methylbutane	CCC(OC)(C)C	*a*	5,6E-12	3,13E-12	-172		231.0	300.0	9,56E-12
37	1,1,1,3,3,3-hexafluoro-2-n-propoxypropane	CCCOC(C(F)(F)F)C(F)(F)F	*a*	2,01E-12	3,11E-12	141		253.0	328.0	8,68E-13
38	4-ethoxy-1,1,1,2,2,3,3,4,5,6,6,6-dodecafluoro-5-(trifluoromethyl)hexane	CCOC(C(C(C(F)(F)F)(F)F)(F)F)(C(C(F)(F)F)(C(F)(F)F)F)F	*a**	2,2E-14						3,44E-14
39	1-ethoxy-1,1,2,2,3,3,4,4,4-nonafluorobutane	CCOC(C(C(C(F)(F)F)(F)F)(F)F)(F)F	*a*	6,5E-14						1,07E-13
40	1-ethoxy-1,1,2,3,3,3-hexafluoro-2-(trifluoromethyl)propane	CCOC(C(C(F)(F)F)(C(F)(F)F)F)(F)F	*a*	7,9E-14						9,83E-14
41	1-ethoxy-1,1,2,3,3,3-hexafluoropropane	CCOC(C(C(F)(F)F)F)(F)F	*a*	1,4E-13						2,33E-13
42	1,1,1,3,3,3-hexafluoro-2-ethoxypropane	CCOC(C(F)(F)F)C(F)(F)F	*a*	1,08E-12	1,86E-12	162		253.0	328.0	2,63E-13
43	1-ethoxy-1,1,2,2-tetrafluoroethane	CCOC(C(F)F)(F)F	*a*	2,2E-13	2,10E-12	670		250.0	430.0	3,65E-13
44	trifluoromethoxyethane	CCOC(F)(F)F	*a*	1,5E-13						4,04E-13
45	1-chloro-2-ethoxyethane	ClCCOCC	*a*	8,3E-12						8,37E-12
46	bis(2-chloroethyl) ether	ClCCOCCCl	*a*	7,6E-12						7,84E-12
47	1,1,1,2,2,3,3,4,4,5,5-undecafluoro-5-methoxypentane	COC(C(C(C(C(F)(F)F)(F)F)(F)F)(F)F)(F)F	*a*	1,2E-14						1,49E-14
48	1,1,1,2,2,3,3,4,4-nonafluoro-4-methoxybutane	COC(C(C(C(F)(F)F)(F)F)(F)F)(F)F	*a*	1,2E-14	1,30E-12	1400		288.0	368.0	1,74E-14
49	1,1,1,2,2,3,4,5,5,5-decafluoro-3-methoxy-4-(trifluoromethyl)pentane	COC(C(C(F)(F)F)(C(F)(F)F)F)(C(C(F)(F)F)(F)F)F	*a*	1,1E-14	5,60E-13	1186		271.0	333.0	1,13E-14
50	2-[difluoro(methoxy)methyl]-1,1,1,2,3,3,3-heptafluoropropane	COC(C(C(F)(F)F)(C(F)(F)F)F)(F)F	*a*	1,2E-14						1,66E-14
51	1,1,1,2,2,3,3-heptafluoro-3-methoxypropane	COC(C(C(F)(F)F)(F)F)(F)F	*a*	1,1E-14	1,40E-12	1440		250.0	430.0	2,17E-14
52	1,1,1,2,3,3-hexafluoro-3-methoxypropane	COC(C(C(F)(F)F)F)(F)F	*a*	2,1E-14						3,58E-14
53	methoxyflurane	COC(C(Cl)Cl)(F)F	*a*	2,06E-13						1,42E-13
54	2-chloro-1,1,2-trifluoro-1-methoxyethane	COC(C(Cl)F)(F)F	*a*	3,8E-14	2,59E-12	1260		273.0	363.0	7,99E-14
55	1,1,1,2,3,3,3-heptafluoro-2-methoxypropane	COC(C(F)(F)F)(C(F)(F)F)F	*a*	1,5E-14	1,30E-12	1330		250.0	430.0	2,03E-14
56	1,1,1,2,2-pentafluoro-2-methoxyethane	COC(C(F)(F)F)(F)F	*a*	1,19E-14	1,18E-12	1370		250.0	300.0	2,99E-14
57	1,1,1,3,3,3-hexafluoro-2-methoxypropane	COC(C(F)(F)F)C(F)(F)F	*a*	2,14E-13	1,24E-12	523,07		253.0	328.0	3,95E-14
58	1,1,1,2-tetrafluoro-2-methoxyethane	COC(C(F)(F)F)F	*a*	1,6E-13	2,05E-12	760		253.0	328.0	6,47E-14
59	1,1,2,2-tetrafluoro-1-methoxyethane	COC(C(F)F)(F)F	*a*	2,2E-14	1,70E-12	1300		250.0	430.0	5,23E-14
60	trifluoro(methoxy)methane	COC(F)(F)F	*a*	1,2E-14	1,84E-12	1500		268.0	381.0	4,82E-14
61	difluoro(methoxy)methane	COC(F)F	*a*	3,5E-14	6,00E-12	1530		253.0	460.0	1,16E-13
62	1,1,1,2,2-pentafluoro-3-methoxypropane	COCC(C(F)(F)F)(F)F	*a*	7,84E-13	2,29E-12	319		263.0	353.0	1,32E-13
63	1,1,2,2-tetrafluoro-3-methoxypropane	COCC(C(F)F)(F)F	*a*	9,61E-13	2,74E-12	312		263.0	353.0	2,07E-13
64	1,1-dichloro-2-methoxyethane	COCC(Cl)Cl	*a*	2,1E-12						2,40E-12
65	1,1,1-trifluoro-2-methoxyethane	COCC(F)(F)F	*a*	6,39E-13	3,51E-12	508		263.0	353.0	2,26E-13

66	1-bromo-2-methoxyethane	COCCBr	*a*	6,3E-12						7,72E-12
67	1,1,3-trimethoxypropane	COCCC(OC)OC	*a*	1,67E-11						1,23E-11
68	1,4-dimethoxybutane	COCCCCOC	*a*	3E-11						2,00E-11
69	1-chloro-2-methoxyethane	COCCCl	*a*	4,75E-12						4,81E-12
70	methyl hypochlorite	COCl	*a*	7E-13	2,40E-12	360		250.0	314.0	3,20E-13
71	fluoro(fluoromethoxy)methane	FCOCF	*a*	6E-14						2,10E-13
72	difluoromethoxy(difluoro)methane	FC(OC(F)F)F	*a*	2,4E-15	1,10E-12	1830		251.0	314.0	5,78E-15
73	difluoromethoxy(trifluoro)methane	FC(OC(F)(F)F)F	*a*	4,9E-16	4,60E-13	2040		298.0	393.0	1,62E-15
74	bis(difluoromethoxy)-difluoromethane	FC(OC(OC(F)F)(F)F)F	*a*	2,4E-15						7,06E-15
75	3-(difluoromethoxy)-1,1,1,2,2-pentafluoropropane	FC(OCC(C(F)(F)F)(F)F)F	*a*	1E-14	1,60E-12	1510		250.0	430.0	2,12E-14
76	3-(difluoromethoxy)-1,1,2,2-tetrafluoropropane	FC(OCC(C(F)F)(F)F)F	*a*	1,6E-14	1,82E-12	1410		250.0	430.0	3,53E-14
77	2-[chloro(difluoro)methoxy]-1,1,1-trifluoroethane	FC(OCC(F)(F)F)(Cl)F	*a*	4E-14	1,60E-12	1100		293.0	410.0	2,59E-14
78	2-(difluoromethoxy)-1,1,1-trifluoroethane	FC(OCC(F)(F)F)F	*a*	1,1E-14	2,90E-12	1660		253.0	460.0	3,43E-14
79	1-(difluoromethoxy)-1,1,2-trifluoroethane	FCC(OC(F)F)(F)F	*a*	5,4E-15	1,11E-12	1588		268.0	308.0	1,99E-14
80	sevoflurane	FCOC(C(F)(F)F)C(F)(F)F	*a*	3,5E-14	8,77E-13	960		241.0	422.0	2,54E-14
81	desflurane	FC(OC(C(F)(F)F)F)F	*a*	4,2E-15	8,15E-13	1570		241.0	298.0	3,84E-15
82	1-(difluoromethoxy)-1,1,2,2-tetrafluoroethane	FC(OC(C(F)F)(F)F)F	*a*	2,7E-15	5,80E-13	1600		253.0	407.0	4,94E-15
83	1,1,1,2,2,3,3,4,4-nonafluoro-4-[3-(1,1,2,2,3,3,4,4,4-nonafluorobutoxy)propoxy]butane	FC(C(C(C(F)(F)F)(F)F)(F)F)(F)F)(OCCCOC(C(C(C(F)(F)F)(F)F)(F)F)(F)F)(F)F)F	*a*	1,3E-13						1,03E-13
84	1,1,1,2,3,3-hexafluoro-3-(2,2,3,3-tetrafluoropropoxy)propane	FC(C(COC(C(C(F)(F)F)F)(F)F)(F)F)(F)F)F	*a*	1,29E-14	2,44E-12	1563		268.0	308.0	1,73E-14
85	1,1,1,2-tetrafluoro-2-(trifluoromethoxy)ethane	FC(C(F)(F)F)OC(F)(F)F	*a*	1,15E-15	3,10E-13	1680		250.0	430.0	1,04E-15
86	1,1,1,2-tetrafluoro-2-(1,1,2,2-tetrafluoroethoxy)ethane	FC(C(OC(C(F)(F)F)F)(F)F)F	*a*	4,1E-15	5,50E-13	1462		267.0	407.0	3,69E-15
87	1,1,1,2,3,3-hexafluoro-3-(trifluoromethoxy)propane	FC(C(OC(F)(F)F)(F)F)C(F)(F)F	*a*	1,55E-15	4,10E-13	1662		270.0	406.0	1,32E-15
88	1,1,2,2-tetrafluoro-1-(trifluoromethoxy)ethane	FC(C(OC(F)(F)F)(F)F)F	*a*	2,1E-15	5,30E-13	1655		269.0	403.0	1,99E-15
89	1,1,2-trifluoro-2-(trifluoromethoxy)ethane	FC(C(OC(F)(F)F)F)F	*a*	6,7E-15						6,66E-15
90	1,1,1,2,3,3-hexafluoro-3-(2,2,3,3,3-pentafluoropropoxy)propane	FC(C(OCC(C(F)(F)F)(F)F)(F)F)(F)F)C(F)(F)F	*a*	6,3E-15	8,46E-13	1460		253.0	328.0	1,10E-14
91	1,1,2,2-Tetrafluoro-3-(1,1,2,2-tetrafluoroethoxy)propane	FC(C(OCC(C(F)F)(F)F)(F)F)F	*d*	1,52E-14						2,25E-14
92	1,1,1,2,3,3-hexafluoro-3-(2,2,2-trifluoroethoxy)propane	FC(C(OCC(F)(F)F)(F)F)C(F)(F)F	*a*	8,7E-15	1,20E-12	1469		268.0	407.0	1,55E-14
93	1,1,2,2-tetrafluoro-1-(2,2,2-trifluoroethoxy)ethane	FC(C(OCC(F)(F)F)(F)F)F	*a*	9,5E-15	1,32E-12	1470		250.0	430.0	2,08E-14
94	1,1,1,2,3,3-hexafluoro-3-[3-(1,1,2,3,3,3-hexafluoropropoxy)propoxy]propane	FC(C(OCCCOC(C(C(F)(F)F)F)(F)F)(F)F)C(F)(F)F	*a*	2,3E-13						2,85E-13
95	1,1,1-trifluoro-2-(2,2,2-trifluoroethoxy)ethane	FC(COCC(F)(F)F)(F)F	*a*	1,4E-13	2,80E-12	890		268.0	409.0	7,09E-14

96	1-(difluoromethoxy)-1,1,2,3,3,3-hexafluoropropane	FC(OC(C(C(F)(F)F)F)(F)F)F	*a*	1,6E-15						3,49E-15
97	enflurane	FC(OC(C(Cl)F)(F)F)F	*a*	1,2E-14	6,73E-13	1200		302.0	422.0	9,97E-15
98	1,1,1,3,3,3-hexafluoro-2-(trifluoromethoxy)propane	FC(OC(C(F)(F)F)C(F)(F)F)(F)F	*a*	3E-16						7,09E-16
99	2-(difluoromethoxy)-1,1,1,3,3,3-hexafluoropropane	FC(OC(C(F)(F)F)C(F)(F)F)F	*a*	2,8E-15	1,03E-12	1760		284.0	398.0	2,68E-15
100	isoflurane	FC(OC(C(F)(F)F)Cl)F	*a*	1,5E-14	1,10E-12	1275		250.0	430.0	7,79E-15
101	1,2-bis(difluoromethoxy)-1,1,2,2-tetrafluoroethane	FC(OC(C(OC(F)F)(F)F)(F)F)F	*a*	4,7E-15						4,70E-15
102	1-(difluoromethoxy)-2-[difluoromethoxy(difluoro)methoxy]-1,1,2,2-tetrafluoroethane	FC(OC(OC(C(OC(F)F)(F)F)(F)F)(F)F)F	*a*	4,6E-15						2,07E-15
103	oxirane	O1CC1	*a*	9,1E-14	1,63E-12	856	2	298.0	435.0	9,57E-13
104	1,4-dioxane	O1CCOCC1	*a*	1,15E-11	6,80E-12	-159		240.0	440.0	3,58E-11
105	1,3,5-trioxane	O1COCOC1	*a*	5,4E-12	1,50E-11	302		292.0	597.0	7,89E-12
106	tetrahydrofuran	C1CCCO1	*a*	1,67E-11	4,77E-12	-375,69	1,20	260.0	1338.0	2,64E-11
107	2-Methyl-1,3-dioxolane	CC1OCCO1	*e*	9,78E-12						1,98E-11
108	oxepane	C1CCCCOC1	*a*	1,8E-11	9,80E-12	-179		263.0	372.0	2,94E-11
109	oxane	C1CCCOC1	*a*	1,2E-11	7,80E-12	-136		263.0	372.0	2,79E-11
110	1,3-dioxepane	C1CCCOCO1	*a*	1,4E-11	6,00E-12	-250		263.0	372.0	4,39E-11
111	oxetane	C1CCO1	*a*	1,03E-11						1,76E-11
112	1,3-dioxane	C1CCOCO1	*a*	1E-11	8,60E-12	-45		240.0	440.0	2,83E-11
113	1,3-dioxolane	C1OCCO1	*a*	1E-11						2,08E-11
114	cineole	CC12CCC(CC1)C(O2)(C)C	*a*	1,04E-11						3,42E-11
115	2-methyloxolane	CC1CCCO1	*a*	2,46E-11	2,57E-12	-673		240.0	400.0	2,41E-11
116	4-methyl-1,3-dioxane	CC1CCOCO1	*a*	1,13E-11						2,49E-11
117	cyclohexene oxide	C1CCC2C(C1)O2	*a*	6,2E-12	6,70E-14	-1349	3,4	251.0	373.0	6,77E-12
118	methyl oxirane	CC1CO1	*a*	4,67E-13	4,67E-13	0		261.0	335.0	1,58E-12
119	2,3-epoxybutane	CC1OC1C	*a***	1,87E-12						2,14E-12
120	ethyl oxirane	CCC1CO1	*a*	1,92E-12	1,70E-14	-1407	4,8	220.0	950.0	2,48E-12
121	1,2-epoxyhexane	CCCCC1CO1	*a*	5,76E-12						4,70E-12
122	2-ethoxy-3,3,4,4,5-pentafluoro-2,5-bis(1,1,1,2,3,3,3-heptafluoropropan-2-yl)oxolane	CCOC1(OC(C(C1(F)F)(F)F)(F)C(C(F)(F)F)(C(F)(F)F)F)C(C(F)(F)F)(C(F)(F)F)F	*a*	5,50E-14						3,12E-14
123	epichlorohydrin	ClCC1CO1	*a*	3,97E-13	1,1E-14	-1082	5,16	230.0	370.0	1,31E-12

[a](McGillen *et al.*, 2020)[5] [b](Metcalf *et al.*, 2025)[6] [c](Dagaut *et al.*, 1989)[7] [d](Tokuhashi, Takizawa, and Kondo, 2024)[8] [e](Stemmler, Mengon, and Kerr, 1996)[9] *Using the relative-rate measurement, no recommendation from the database (McGillen *et al.* (2020)[5]). **Assuming trans conformation.

SI-2: Additional plots to Figure 4

The unique van der Waals complexes that can be formed for the full enumeration of acyclic alkyl ethers of formula $C_nO_{\leq n-1}H_{2n+2}$, where $2 \leq n \leq 8$, are presented per type of complex formed. The list of molecules was generated using MOLGEN software.

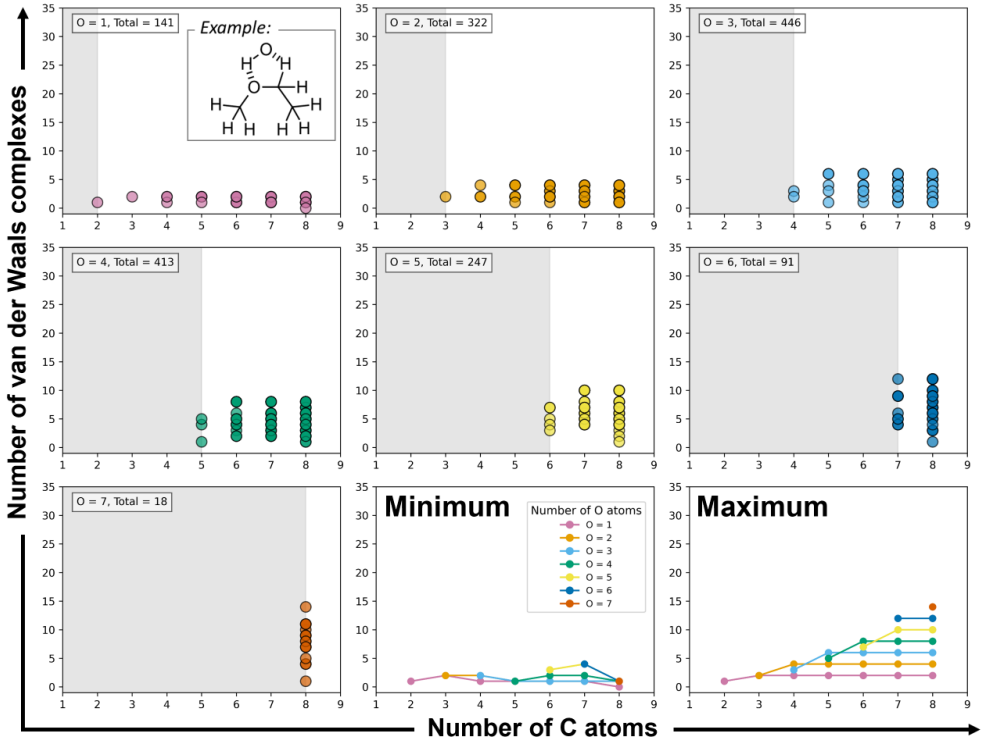


Figure SI-2a: The dependence of the number of possible unique van der Waals complexes considered upon carbon and oxygen number for a fully enumerated list of acyclic alkyl ethers, $C_nO_{\leq n-1}H_{2n+2}$, where $2 \leq n \leq 8$ for 5-membered van der Waals complexes.

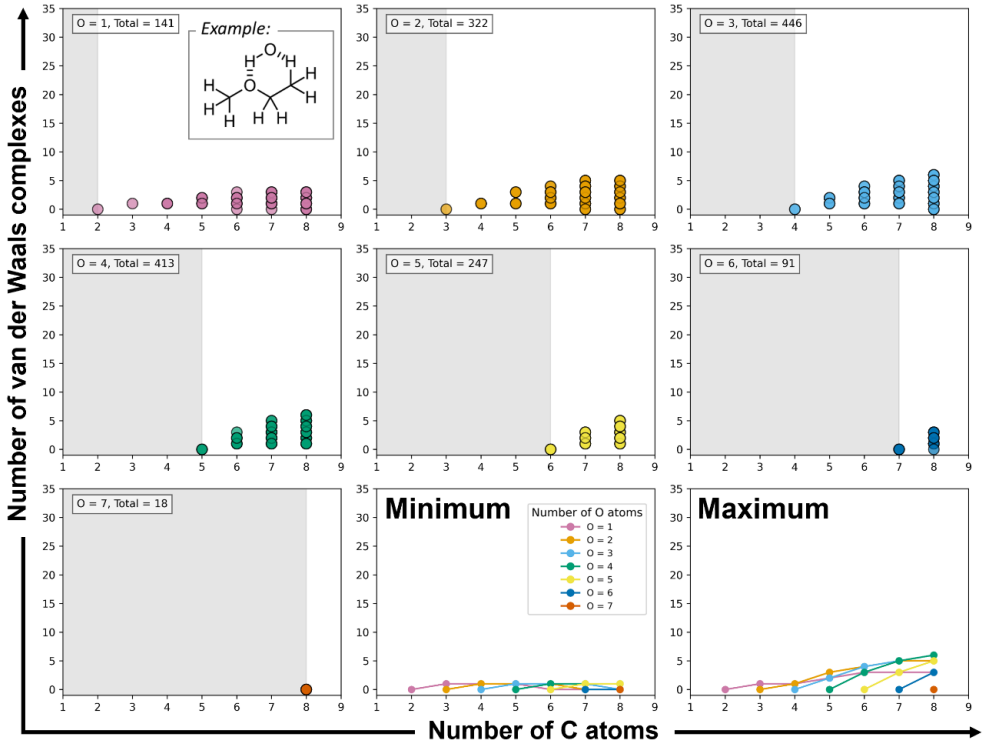


Figure SI-2b: The dependence of the number of possible unique van der Waals complexes considered upon carbon and oxygen number for a fully enumerated list of acyclic alkyl ethers, $C_nO_{\leq n-1}H_{2n+2}$, where $2 \leq n \leq 8$ for 6-membered van der Waals complexes.

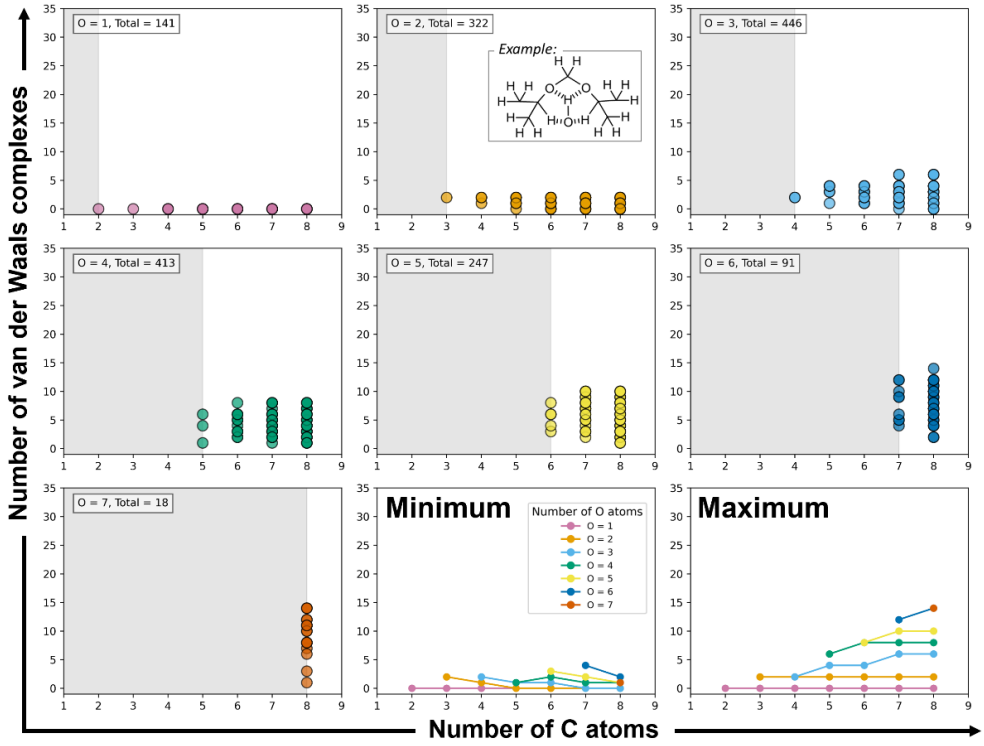


Figure SI-2c: The dependence of the number of possible unique van der Waals complexes considered upon carbon and oxygen number for a fully enumerated list of acyclic alkyl ethers, $C_nO_{\leq n-1}H_{2n+2}$, where $2 \leq n \leq 8$ for bicyclic 5-membered van der Waals complexes.

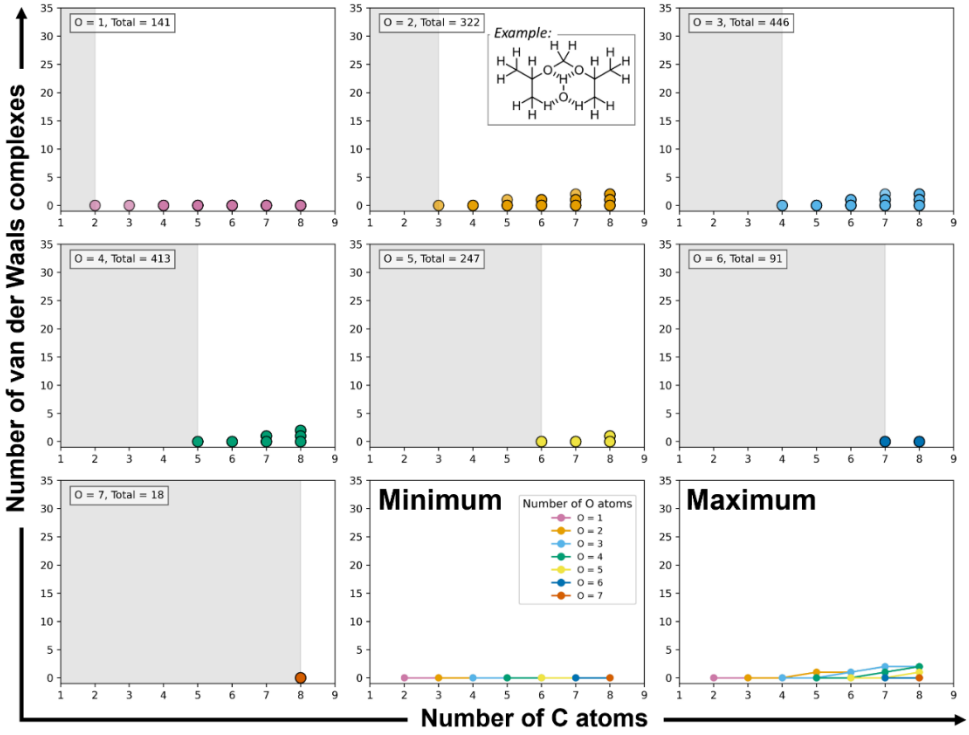


Figure SI-2d: The dependence of the number of possible unique van der Waals complexes considered upon carbon and oxygen number for a fully enumerated list of acyclic alkyl ethers, $C_nO_{\leq n-1}H_{2n+2}$, where $2 \leq n \leq 8$ for bicyclic 6-membered van der Waals complexes.

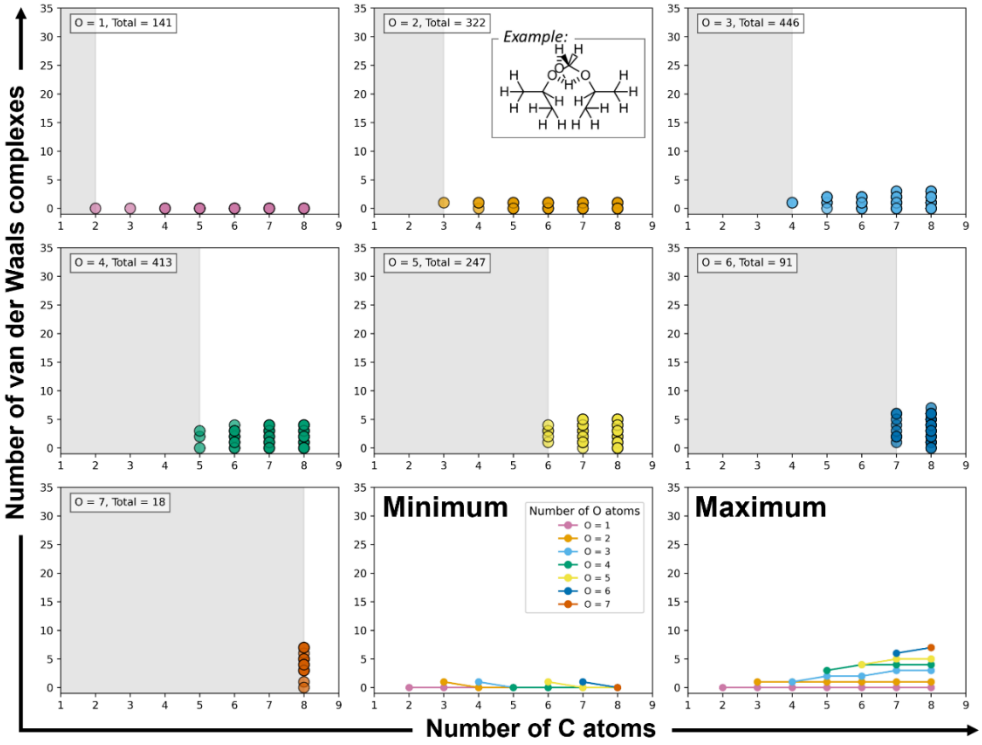


Figure SI-2e: The dependence of the number of possible unique van der Waals complexes considered upon carbon and oxygen number for a fully enumerated list of acyclic alkyl ethers, $C_nO_{\leq n-1}H_{2n+2}$, where $2 \leq n \leq 8$ for bicyclic 5-membered van der Waals complexes on secondary carbons.

SI-3: Formula to predict *k*(*T*) for alkanes and haloalkanes:

The calculations can be found in the spreadsheet "**SI_calculations.xlsx**".

Below are the methodology and excel formula to copy/paste to derive the parameters *A*, *B*, *n* for atom C_i used in (Eq. 1):

$$k_{\text{total}}(T) = \sum_i \kappa_i(T) A_i \exp\left(-\frac{B_i}{T}\right)\left(\frac{T}{298}\right)^{n_i} = \sum_i \kappa_i(T)\, k_{\text{base,i}}(T) \qquad 1.$$

to predict site-specific temperature dependent rate coefficients using the original E-state method (see below Table SI-2 and Table SI-3 from McGillen et al. (2024) (Tables 1 and 2 in the original paper).

Table SI-2: Fitting parameters for making site-specific estimates of room-temperature rate coefficients using the E-state method (McGillen et al., 2024).

Hydrogen count	*a*	*b*	*c*
3 (primary)	0.235348	0.448094	15.226433
2 (secondary)	0.079290	0.770329	13.470563
1 (tertiary)	0.051234	0.723300	12.452133

Use Table SI-3 to get $k_{298,i} = n_{Hi} \times 10\text{^}(a_{298,i} S_i^2 + b_{298,i} S_i - c_{298,i})$ (Eq. 3) with a_{298}, b_{298} and c_{298} taken from Table SI-2.

Table SI-3: Fitting parameters for making site-specific temperature-dependent estimates of rate coefficients using the E-state method (McGillen et al., 2024).

Polynomial fitting parameters			
Hydrogen count	a	b	c
3 (primary)	0.499883684	3.4716×10^{-8}	15.02936825
2 (secondary)	0.071820619	0.732006578	13.37605256
1 (tertiary)	0.044353068	0.685568344	12.48928548
Temperature-dependent fitting parameters			
m	d	f	g
−199.2590651	−2242.434844	0.797686801	2.911224679

Use Table SI-3 to get the factor $B = E_a/R = m \times (a_{temp,i}\, S_i^2 + b_{temp,i}\, S_i - c_{temp,i}) + d_{temp,i}$ with m, a_{temp}, b_{temp}, c_{temp} and d_{temp} taken from Table SI-3 and R = 0.00831446261815324 J mol^{-1} K, the factor $A = k_{298} \times \exp(B/298)$ (Eq. 10), and the factor $n = f + E_a/g$ (Eq. 12) with f and g as in Table SI-3.

To obtain each Arrhenius parameter and k_{base}(T) using S_Ci and T in Excel:

Hydrogen count: H_s = 3 (primary)

B3 = -199.2590651 * (0.499883684 * S_Ci^2 + 3.4716 * 10^-8 * S_Ci - 15.02936825) - 2242.434844
A3 = 3 * 10 ^ (0.235348 * S_Ci^2 + 0.448094 * S_Ci - 15.226433) * EXP(B3 / 298)
n3 = 0.797686801 + B3 * 0.00831446261815324 / 2.91122467932999
k_{base} = A3 * EXP(-B3/T)*(T/298)^n3

Hydrogen count: H_s = 2 (secondary)

B2 = -199.2590651 * (0.071820619 * S_Ci^2 + 0.732006578 * S_Ci - 13.37605256) - 2242.434844
A2 = 2* 10 ^ (0.079290 * S_Ci^2 + 0.770329 * S_Ci - 13.470563) * EXP(B2 / 298)
n2 = 0.797686801 + B2 * 0.00831446261815324 / 2.91122467932999
k_{base} = A2 * EXP(-B2/T)*(T/298)^n2

Hydrogen count: H_s = 1 (tertiary)

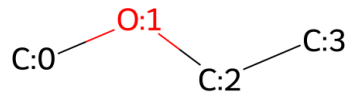
B1 = -199.2590651 * (0.044353068 * S_Ci^2 + 0.685568344 * S_Ci - 12.48928548) - 2242.434844
A1 = 10 ^ (0.051234 * S_Ci^2 + 0.723300 * S_Ci - 12.452133) * EXP(B1 / 298)
n1 = 0.797686801 + B1 * 0.00831446261815324 / 2.91122467932999
k_{base} = A1 * EXP(-B1/T)*(T/298)^n1

SI-4: Calculation of κ_i for the example molecules in Figure 3 at room-temperature (298K):

The calculations can be found in the spreadsheet "**SI_calculations.xlsx**".

The values of the E-states are in the code's output and can be calculated as described in the paper. Units are those specified in the paper.

Molecule (1): COCC



For the molecule M1, each reactive site has one possible complex configuration (see details on the substitution type and complex configuration in legend of the Figure 3).

Site 1, Atom C0: correction for complex (1)A, involving atom O_1.

$$\kappa_1 = \alpha_{\text{5-mem., prim}} \cdot \log S(O_1) \cdot \exp\left(\beta_{\text{5-mem., prim}}/T\right)$$

SI(C_0) = 1.6806 and $\boldsymbol{k_{base,1}}$ **= 4.66×10^{-14}** with Arrhenius parameter for H_s=3: *A*=2.26×10^{-13}, *B*=470.99, *n*=2.14.
SI(O_1) = 4.5417, $\boldsymbol{\kappa_1}$ **= 17.301** and $\boldsymbol{k_{tot,1}}$ **= 8.06×10^{-13}**.

Site 2, Atom C2: correction for complex (1)B, involving atom O_1.

$$\kappa_2 = \alpha_{\text{5-mem., sec}} \cdot \log S(O_1) \cdot \exp\left(\beta_{\text{5-mem., sec}}/T\right)$$

SI(C_2) = 0.8194 and $\boldsymbol{k_{base,2}}$ **= 3.27×10^{-13}** with Arrhenius parameter for H_s=2: *A*=8.77×10^{-13}, *B*=293.73, *n*=1.64.
SI(O_1) = 4.5417, $\boldsymbol{\kappa_2}$ **= 9.617** and $\boldsymbol{k_{tot,2}}$ **= 3.15×10^{-12}**.

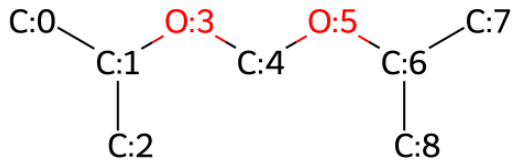
Site 3, Atom C3: correction for complex (1)C, involving atom O_1.

$$\kappa_3 = \alpha_{\text{6-mem., prim}} \cdot \log S(O_1) \cdot \exp\left(\beta_{\text{6-mem., prim}}/T\right)$$

SI(C_3) = 1.9583 and $k_{base,3}$ = 1.07×10^{-13} with Arrhenius parameter for H_s=3: *A*=3.72×10^{-13}, *B*=370.31, *n*=1.86.
SI(O_1) = 4.5417, $\boldsymbol{\kappa_3}$ **= 8.716** and $\boldsymbol{k_{tot,3}}$ **= 9.36×10^{-13}**.

> k_{tot} = 4.89×10^{-12}

Molecule (2): CC(C)OCOC(C)C



For the molecule (2), each reactive site can have one or more possible complex configuration (see details on the substitution type and complex configuration in legend of the Figure 3).
Atom 0, 2, 7 and 8: because the molecule is symmetrical, these reactive sites are identical.
Atom 1 and 6: because the molecule is symmetrical, these reactive sites are identical.
The E-state values of O_3 and O_5 are also equal.

Site 1, Atoms 0/2/7/8: This site forms monocyclic complex (2)C with O_3 (= O_5) and bicyclic complex (2)B with O_3 and O_5. Following the priority rules, since they are all 6-membered complexes, this results in correction for bicyclic complex (2)B with O_3 and O_5.

$$\kappa_1 = \alpha_{\text{6-mem., prim}} \cdot \log S(O_3) \cdot \exp\left(\beta_{\text{6-mem., prim}}/T\right) + \alpha_{\text{6-mem., prim}} \cdot \log S(O_5) \cdot \exp\left(\beta_{\text{6-mem., prim}}/T\right)$$
$$= \alpha_{\text{6-mem., prim}} \cdot \exp\left(\beta_{\text{6-mem., prim}}/T\right) \cdot [\log S(O_3) + \log S(O_5)]$$

SI(C_0) = 1.989769 = SI(C_2) = SI(C_7) = SI(C_8) and $\boldsymbol{k_{base,1}}$ **= 1.19 ×10^{-13}** with Arrhenius parameter for H_s=3: *A*=3.94×10^{-13}, *B*=357.94, *n*=1.82.
SI(O_3) = 5.13042, $\boldsymbol{\kappa_1}$ **= 18.837** and $\boldsymbol{k_{tot,1}}$ **= 2.23 ×10^{-12} =** $\boldsymbol{k_{tot,2}}$ **=** $\boldsymbol{k_{tot,7}}$ **=** $\boldsymbol{k_{tot,8}}$.
Note that the site-specific rate on the terminal carbon in the molecule is thus equal to **4 × 2.23 × 10^{-12} = 8.94× 10^{-12}.**

Site 2, Atoms 1 and 6: Because the molecule is symmetrical, these reactive sites are identical. This site forms monocyclic complex (2)A with O_3 (= O_5) and bicyclic complex (2)F with O_3 and O_5. Following the priority rules, since they are all 5-membered complexes, this results in correction for bicyclic complex (2)F with O_3 and O_5.

$$\kappa_2 = \alpha_{\text{5-mem., tert}} \cdot \exp\left(\beta_{\text{5-mem., tert}}/T\right) \cdot [\log S(O_3) + \log S(O_5)]$$

SI(C_1) = 0.267355 = SI(C_6) and $\boldsymbol{k_{base,2}}$ **= 5.56 ×10^{-13}** with Arrhenius parameter for H_s=1: *A*=1.12×10^{-12}, *B*=209.01, *n*=1.39.
SI(O_3) = 5.13042, $\boldsymbol{\kappa_2}$ **= 2.031** and $\boldsymbol{k_{tot,2}}$ **= 1.13×10^{-12}**.
Note that the site-specific rate on the tertiary carbon in the molecule is thus equal to **2 × 1.13 × 10^{-12} = 2.26 × 10^{-12}.**

Site 3, Atom C4: monocyclic complex (2)E with O_3 (= O_5) and bicyclic complex (2)D with O_3 and O_5. Following the priority rules, since they are all 5-membered complexes, this results in correction for bicyclic complex (2)D with O_3 and O_5.

$$\kappa_3 = \alpha_{\text{5-mem., sec}} \cdot \exp\left(\beta_{\text{5-mem., sec}}/T\right) \cdot [\log S(O_3) + \log S(O_5)]$$

SI(C_4) = 0.412038 and $\boldsymbol{k_{base,3}}$ **= 1.45 ×10^{-13}** with Arrhenius parameter for H_s=2: *A*=4.86×10^{-13}, *B*=360.34, *n*=1.83.
SI(O_3) = 5.13042, $\boldsymbol{\kappa_3}$ **= 20.784** and $\boldsymbol{k_{tot,3}}$ **= 3.01 ×10^{-12}**.

> k_{tot} = 1.42×10^{-11}

SI-5: Experimental and predicted temperature-dependent (190–1500K) rate coefficients for the dataset studied, using all the predictive methods figuring in Figure 7, when existing.

See Excel file "**SI_k298_kT_values.xlsx**".

SI-6: Additional plot to Figure 8

The estimates of the method of Jenkin *et al*. (2018) are plotted together with the estimations of the other approaches; the application temperature range (250–400K) is highlighted in green, and values outside this range are extrapolated.

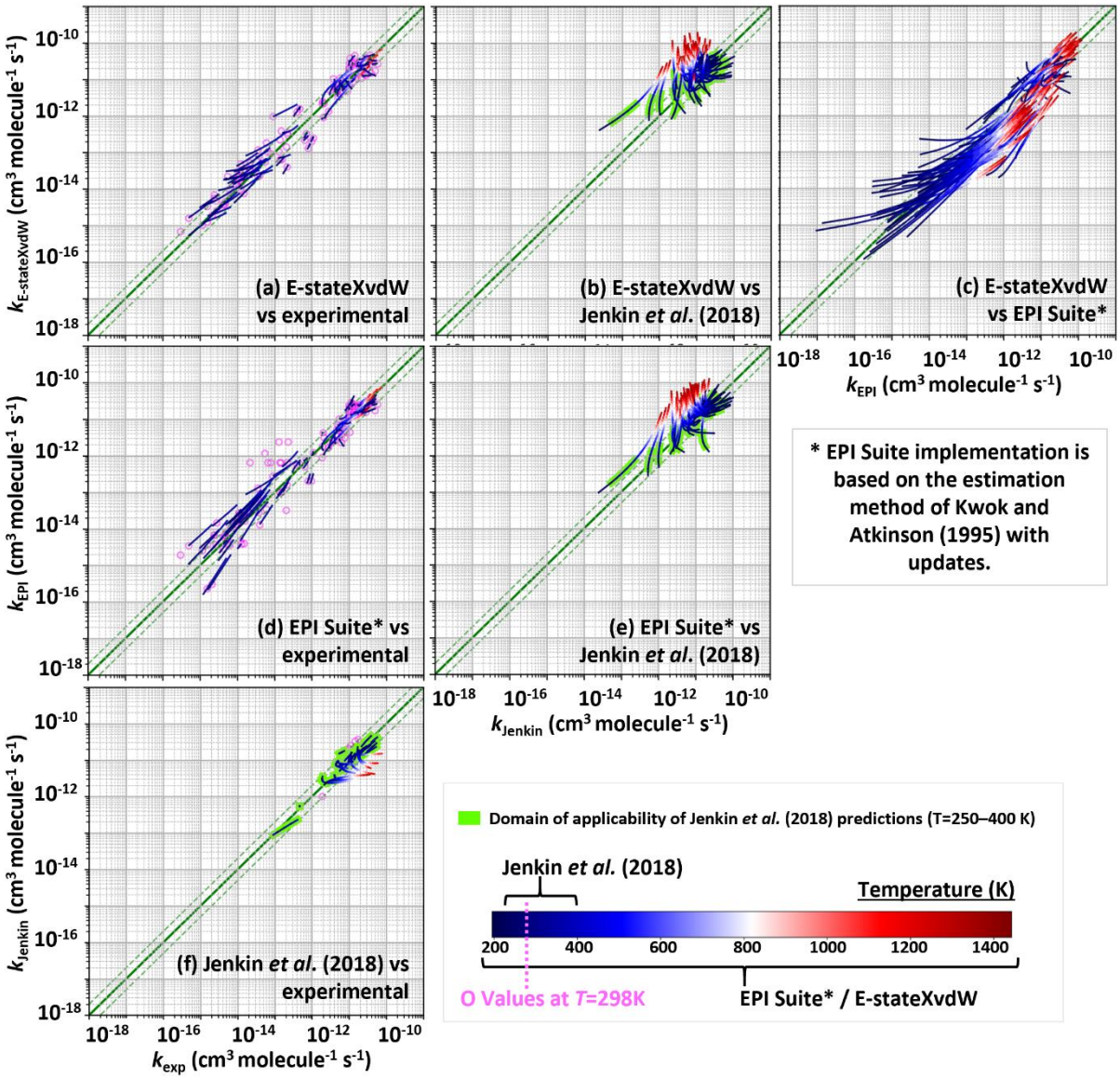


Figure SI-6: Temperature-dependent predictions of $k(T)$ based on the E-stateXvdW method (panel (a), (b) and (f)), the Kwok and Atkinson (1995)[2] approach (implemented in EPI Suite[1]) (panel (d), (e) and (f)), and the Jenkin *et al*. (2018)[4] method (panel (b), (c) and (d)), plotted against all available temperature-dependent experimental data. The extrapolation of Jenkin's method over the temperature range not covered by the original model are plotted, and the applicability domain of the method is highlighted in green.

SI-7: Intercomparison of the estimates between each predictive method and ratio with experimental data

The $k(T)$ estimates obtained, where available, using the 3 temperature-dependent SARs discussed in the main text (Kwok and Atkinson (as implemented in EPI Suite), Jenkin *et al.* (2018), and the E-stateXvdW approach) are presented alongside experimental data (McGillen *et al.*, 2020). This allows for a direct comparison of the performance of the different estimation techniques. For example, in

cases where experimental data are lacking, our method can still be compared to EPI Suite predictions, which cover the full dataset and temperature range (~190–1500 K).

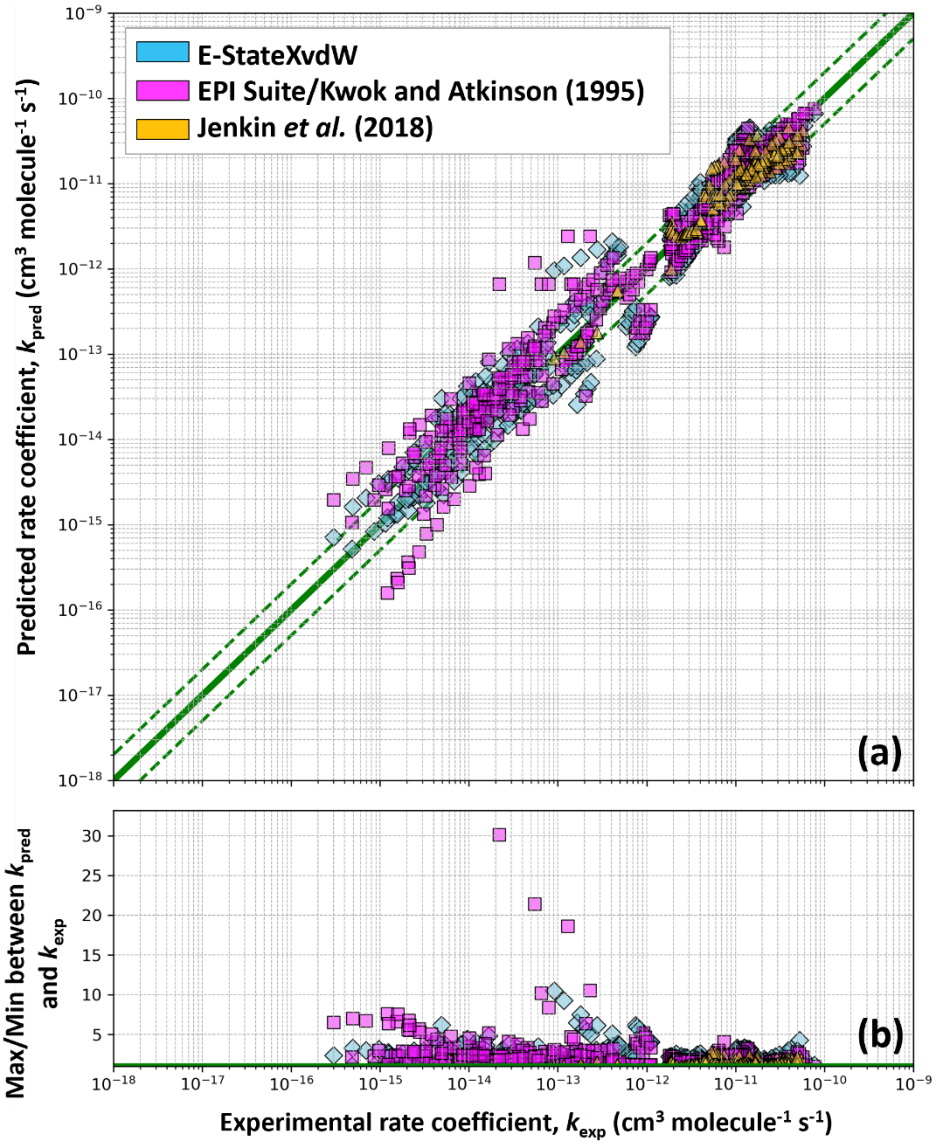


Figure SI-7a: (a) Temperature-dependent predictions of $k(T)$ based on the E-stateXvdW method, the Kwok and Atkinson (1995)[2] approach (implemented in EPI Suite[1]) and the Jenkin *et al.* (2018)[4] method, plotted against all available temperature-dependent experimental data. Ratios against x-axis are plotted in panel (b).

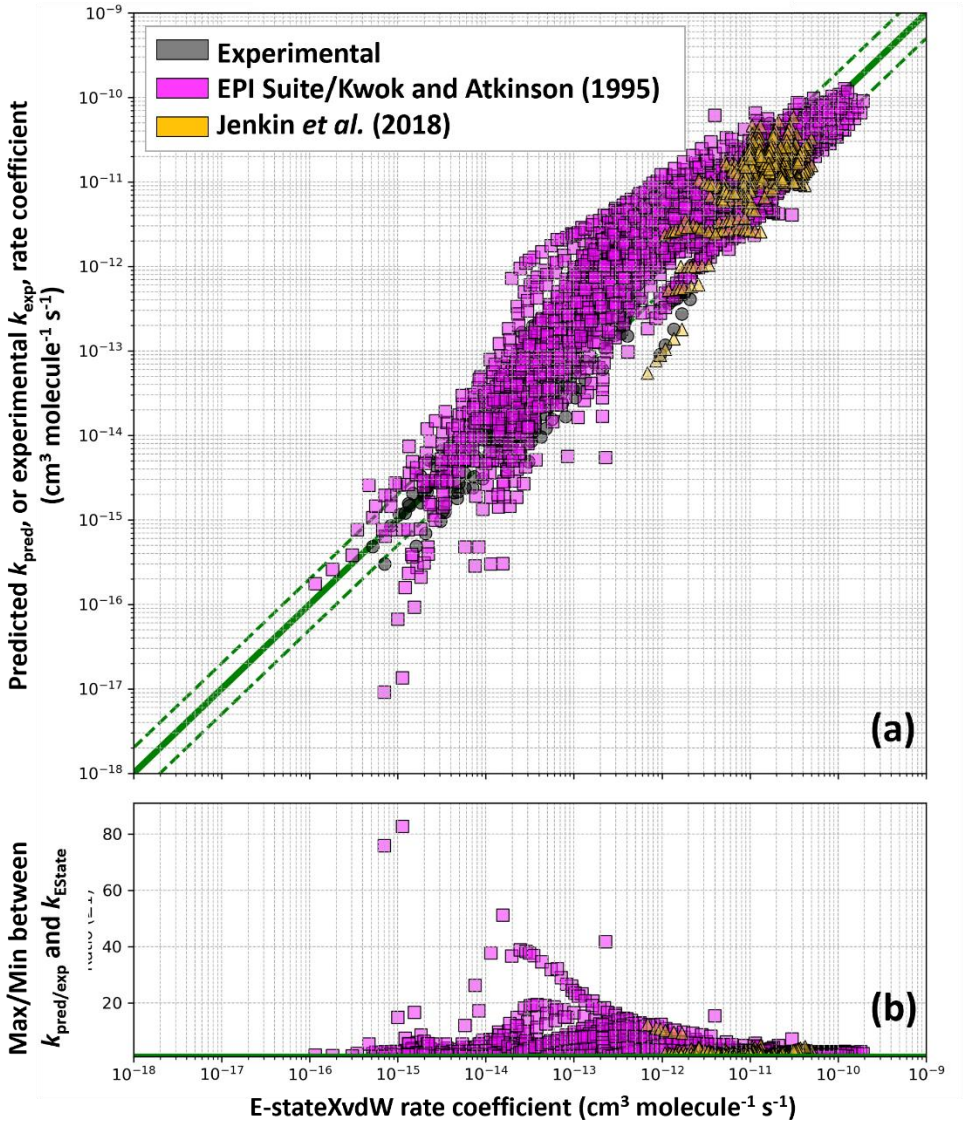


Figure SI-7b: (a) Temperature-dependent measurements and predictions of $k(T)$ based on the Kwok and Atkinson (1995)[2] approach (implemented in EPI Suite[1]) and the Jenkin *et al*. (2018)[4] method, plotted against all available temperature-dependent E-stateXvdW predictions. Ratios against *x*-axis are plotted in panel (b).

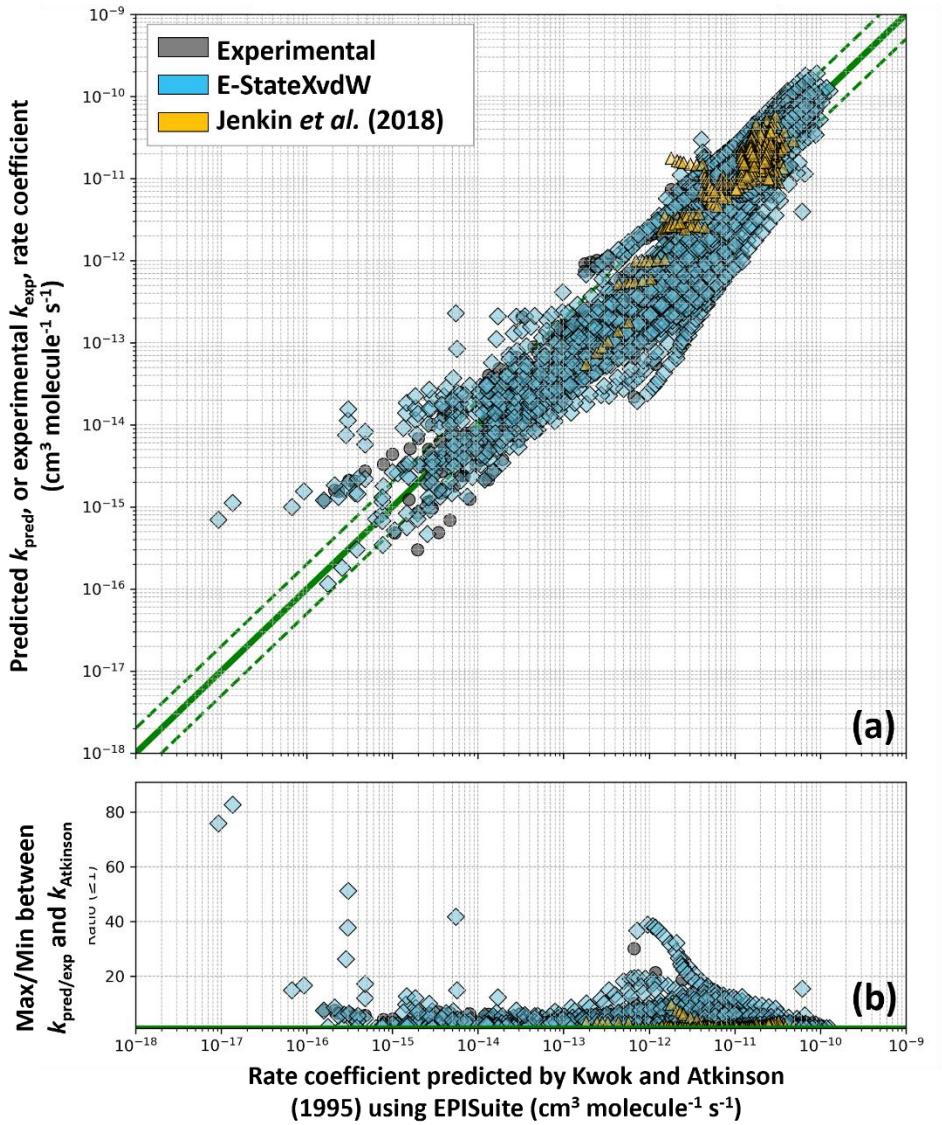


Figure SI-7c: (a) Temperature-dependent measurements and predictions of $k(T)$ based on the E-stateXvdW method and the Jenkin *et al*. (2018)[4] method, plotted against all available temperature-dependent predictions using the Kwok and Atkinson (1995)[2] approach (implemented in EPI Suite[1]). Ratios against *x*-axis are plotted in panel (b).

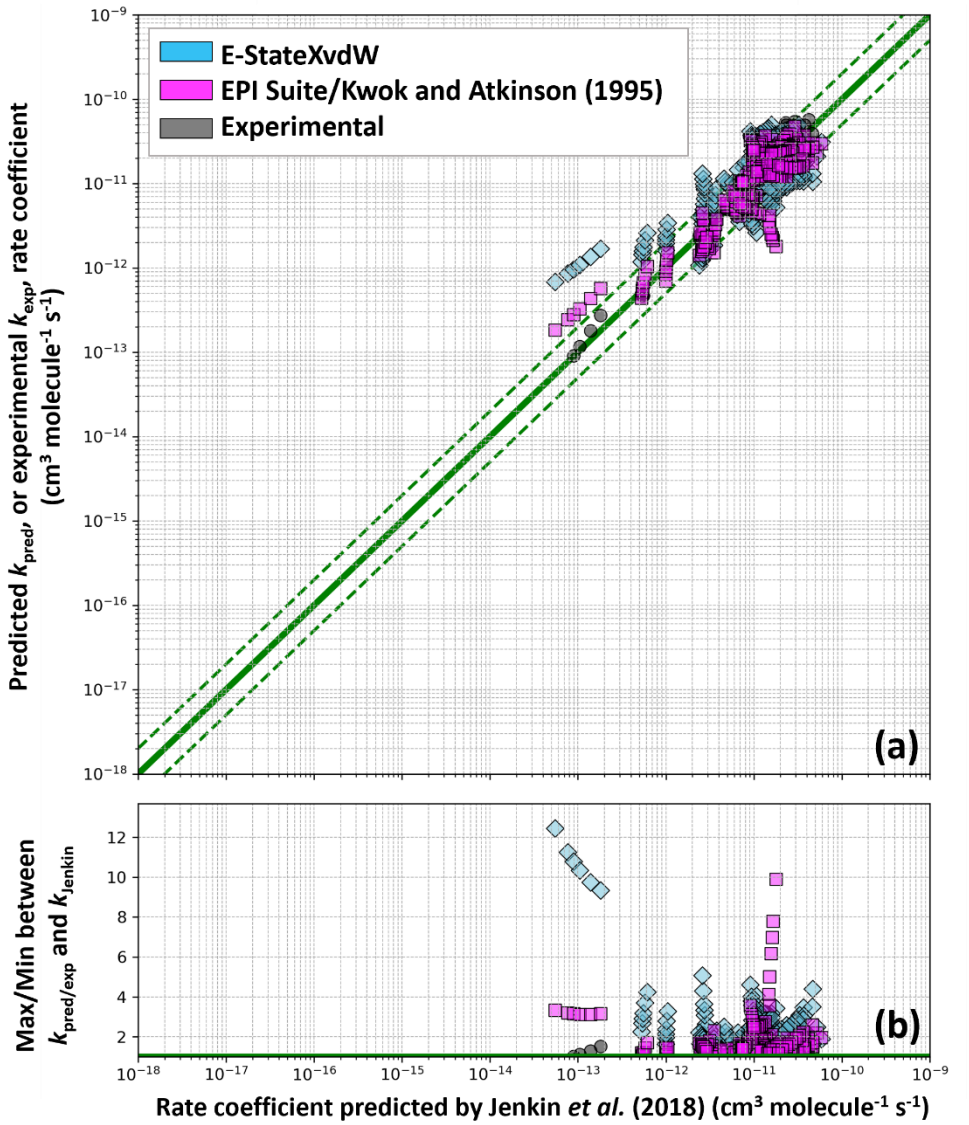


Figure SI-7d: (a) Temperature-dependent measurements and predictions of $k(T)$ based on the Kwok and Atkinson (1995)[2] approach (implemented in EPI Suite[1]) and E-stateXvdW approach, plotted against all available temperature-dependent predictions using the Jenkin *et al*. (2018)[4] method. Ratios against *x*-axis are plotted in panel (b).

SI-8: Code of the E-stateXvdW method

See python file provided "**E-state_kT.py**". Before running, read the **READ_ME.txt** file. Before running, please read the **READ_ME.txt** file. Ensure that the input file (**smiles.txt**) is correctly formatted and that your Python environment has all required libraries installed, as specified in the **READ_ME.txt** file. The user can compare and verify their outputs with those provided for the "Shortened version" @298K and the "Detailed version" @195K for the list of SMILES provided.

For any questions, please contact: lisa.michelat@cnrs-orleans.fr / lisa.michelat@hotmail.fr

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