Supplemental information for:

Computation of Rate Coefficients in Solutions Based on Transition State Theory Combined with a Heuristically Corrected Polarizable Continuum Model: Intermolecular Diels-Alder Reactions as Case Studies

Yu-ichiro Izato,*[a] Mitsuo Koshi,[b] and Atsumi Miyake [a]

[a] Graduate School of Information and Environment Sciences, Yokohama National University

79-7 Tokiwadai, Hodogaya-ku, Yokohama, Kanagawa 240-8501, Japan

Phone: +81-45-339-3992

[b] Professor Emeritus, The University of Tokyo

7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8654, Japan.

*Corresponding address : izato-yuichiro-tk@ynu.ac.jp

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Table S1. Cartesian coordination for all molecules investigated in this study.

solute	solvent	coordination			
cyclopentadiene	Ethanol	C	-1.17321500	-0.28713400	-0.00008300
		C	-0.73895300	0.98437900	-0.00003600
		C	0.72908500	0.99166700	0.00005700
		C	1.17599900	-0.27540600	0.00006600
		H	-2.20295200	-0.61899300	-0.00013900
		H	-1.35810000	1.87270500	-0.00006000
		H	1.33928000	1.88616200	0.00010500
		H	2.20902700	-0.59686300	0.00010700
		C	0.00607100	-1.21272700	-0.00000900
		H	0.00935700	-1.87382500	0.87643400
		H	0.00947200	-1.87386700	-0.87641800
cyclopentadiene	THF	C	-1.17563000	-0.27875700	-0.00007100
		C	-0.73174000	0.98949800	-0.00004000
		C	0.73584700	0.98645900	0.00004700
		C	1.17447400	-0.28363500	0.00006800
		H	-2.20755200	-0.60350800	-0.00013300
		H	-1.34464100	1.88212800	-0.00007300
		H	1.35246100	1.87653000	0.00008700
		H	2.20502900	-0.61270000	0.00012800
		C	-0.00253100	-1.21307200	-0.00000500
		H	-0.00396400	-1.87270900	0.87697900
		H	-0.00386000	-1.87270200	-0.87699400
cyclopentadiene	Toluene	C	-1.17546500	-0.27917100	-0.00007100
		C	-0.73208200	0.98875000	-0.00004000
		C	0.73517100	0.98646700	0.00004700
		C	1.17460000	-0.28283900	0.00006900
		H	-2.20730100	-0.60391200	-0.00013300
		H	-1.34565600	1.88078600	-0.00007300
		H	1.35153800	1.87657700	0.00008700
		H	2.20540700	-0.61083200	0.00012800
		C	-0.00190600	-1.21307000	-0.00000500
		H	-0.00299700	-1.87172400	0.87774500
		H	-0.00289300	-1.87171700	-0.87775900
cyclopentadiene	Cyclohexane	C	-1.17544100	-0.27922600	-0.00007100

		C	-0.73212900	0.98861600	-0.00004000
		C	0.73505900	0.98645000	0.00004700
		C	1.17462100	-0.28270600	0.00006800
		H	-2.20726500	-0.60394400	-0.00013300
		H	-1.34581600	1.88054600	-0.00007300
		H	1.35139600	1.87655200	0.00008700
		H	2.20546800	-0.61051100	0.00012800
		C	-0.00180900	-1.21306500	-0.00000500
		H	-0.00284700	-1.87153200	0.87789100
		H	-0.00274300	-1.87152600	-0.87790500
TS_A	Ethanol	C	1.87332500	-0.80044800	0.46655400
		H	1.70761400	-1.27173500	1.43630000
		H	2.82299900	-1.18770900	0.06962300
		C	0.71325600	0.11528000	-1.35845900
		H	0.24303100	0.19325700	-2.32828900
		C	0.78228800	-1.04923900	-0.56006400
		H	0.67137400	-2.03370500	-1.00358600
		C	1.36442900	1.17094800	-0.66774900
		H	1.34950300	2.20910000	-0.97647400
		C	1.91876600	0.69822200	0.48431400
		H	2.45402900	1.28221200	1.22141300
		C	-0.71325600	0.11527900	1.35845900
		C	-0.78228800	-1.04923900	0.56006400
		C	-1.91876500	0.69822300	-0.48431300
		H	-0.24303100	0.19325600	2.32828900
		H	-0.67137400	-2.03370600	1.00358500
		H	-2.45402800	1.28221300	-1.22141300
		C	-1.36442900	1.17094800	0.66774900
		H	-1.34950200	2.20910000	0.97647500
		C	-1.87332500	-0.80044800	-0.46655400
		H	-1.70761400	-1.27173500	-1.43630000
		H	-2.82299900	-1.18770800	-0.06962400
TS_A	THF	C	-0.00399800	1.93088100	-0.80103300
		H	0.97644600	2.00638500	-1.27344500
		H	-0.62099200	2.75540600	-1.18683100
		C	-1.49080900	0.36174600	0.11584600

		H	-2.31739600	-0.32976500	0.19462900
		C	-0.73474900	0.62298800	-1.04913000
		H	-1.13874700	0.40726000	-2.03324000
		C	-0.97783600	1.16092500	1.17124800
		H	-1.27259900	1.07101100	2.20958600
		C	0.00399800	1.97897700	0.69774000
		H	0.58905500	2.67753000	1.28126900
		C	1.49080900	-0.36174600	0.11584600
		C	0.73474900	-0.62298800	-1.04913000
		C	-0.00399800	-1.97897700	0.69774000
		H	2.31739600	0.32976500	0.19462900
		H	1.13874700	-0.40726000	-2.03324000
		H	-0.58905500	-2.67753000	1.28126900
		C	0.97783600	-1.16092500	1.17124800
		H	1.27259900	-1.07101100	2.20958600
		C	0.00399800	-1.93088100	-0.80103300
		H	-0.97644600	-2.00638500	-1.27344500
		H	0.62099200	-2.75540600	-1.18683100
TS_A	Toluene	C	-1.87371800	-0.80029800	-0.46688100
		H	-1.70751400	-1.27322500	-1.43597900
		H	-2.82468200	-1.18388000	-0.06965300
		C	-0.71524400	0.11490200	1.35834800
		H	-0.24894800	0.19305200	2.32988100
		C	-0.78467500	-1.04954900	0.56148900
		H	-0.67516400	-2.03380500	1.00606100
		C	-1.36350300	1.17088100	0.66572200
		H	-1.34802500	2.20883600	0.97427800
		C	-1.91603800	0.69845900	-0.48665900
		H	-2.45022400	1.28265100	-1.22416100
		C	0.71524400	0.11490200	-1.35834800
		C	0.78467500	-1.04954900	-0.56148900
		C	1.91603800	0.69845900	0.48665900
		H	0.24894800	0.19305200	-2.32988100
		H	0.67516400	-2.03380500	-1.00606100
		H	2.45022400	1.28265100	1.22416100
		C	1.36350300	1.17088100	-0.66572200

		H	1.34802500	2.20883600	-0.97427800
		C	1.87371800	-0.80029800	0.46688100
		H	1.70751400	-1.27322500	1.43597900
		H	2.82468200	-1.18388000	0.06965300
TS_A	Cyclohexane	C	-1.87374300	-0.80026500	-0.46695600
		H	-1.70745400	-1.27341600	-1.43596000
		H	-2.82489700	-1.18334400	-0.06971700
		C	-0.71551700	0.11484100	1.35834400
		H	-0.24984000	0.19296100	2.33015200
		C	-0.78498700	-1.04959100	0.56166600
		H	-0.67566100	-2.03382500	1.00635700
		C	-1.36338000	1.17086200	0.66546600
		H	-1.34788100	2.20878200	0.97403000
		C	-1.91562000	0.69850400	-0.48699500
		H	-2.44964000	1.28273400	-1.22455600
		C	0.71551700	0.11484100	-1.35834400
		C	0.78498700	-1.04959100	-0.56166600
		C	1.91562000	0.69850400	0.48699500
		H	0.24984000	0.19296100	-2.33015200
		H	0.67566100	-2.03382500	-1.00635700
		H	2.44964000	1.28273400	1.22455600
		C	1.36338000	1.17086200	-0.66546600
		H	1.34788100	2.20878200	-0.97403000
		C	1.87374300	-0.80026500	0.46695600
		H	1.70745400	-1.27341600	1.43596000
		H	2.82489700	-1.18334400	0.06971700
cyclohexadiene	Ethanol	C	0.11052700	1.41850600	0.06324400
		C	1.25371100	0.72571500	0.11060900
		C	1.25404100	-0.72516600	-0.11055100
		C	0.11114500	-1.41843300	-0.06335700
		H	0.11105700	2.49657800	0.19018800
		H	2.19932000	1.22658700	0.29098700
		H	2.19985100	-1.22565600	-0.29097500
		H	0.11214500	-2.49650400	-0.19035700
		C	-1.18879600	-0.72358800	0.25032400
		H	-1.33181000	-0.73739500	1.34138600

		H	-2.03325000	-1.27040200	-0.17559500
		C	-1.18915900	0.72305700	-0.25027300
		H	-2.03380900	1.26952800	0.17569300
		H	-1.33231800	0.73671200	-1.34129900
cyclohexadiene	Chloroform	C	0.11076000	1.41827600	0.06340600
		C	1.25337100	0.72519800	0.11091300
		C	1.25336800	-0.72520300	-0.11091300
		C	0.11075500	-1.41827700	-0.06340600
		H	0.11156500	2.49621400	0.19105100
		H	2.19882400	1.22580800	0.29243900
		H	2.19881900	-1.22581700	-0.29243800
		H	0.11155500	-2.49621500	-0.19105000
		C	-1.18862700	-0.72289400	0.25142300
		H	-1.32934300	-0.73457800	1.34279300
		H	-2.03404800	-1.26982600	-0.17274700
		C	-1.18862400	0.72289800	-0.25142400
		H	-2.03404300	1.26983400	0.17274700
		H	-1.32934000	0.73458300	-1.34279300
cyclohexadiene	benzene	C	0.11070500	1.41810700	0.06346900
		C	1.25295700	0.72501100	0.11119400
		C	1.25294900	-0.72502400	-0.11119500
		C	0.11069000	-1.41810800	-0.06346800
		H	0.11152200	2.49591900	0.19168500
		H	2.19815700	1.22559200	0.29370800
		H	2.19814300	-1.22561600	-0.29370800
		H	0.11149600	-2.49592100	-0.19168400
		C	-1.18832300	-0.72254100	0.25235000
		H	-1.32722600	-0.73250700	1.34395700
		H	-2.03443000	-1.26972800	-0.17038000
		C	-1.18831500	0.72255300	-0.25235000
		H	-2.03441700	1.26974900	0.17038000
		H	-1.32721800	0.73252100	-1.34395700
nitrosobenzene	Ethanol	C	1.26978100	-1.33231400	-0.00001700
		C	-0.09394100	-1.09979600	0.00000300
		C	-0.55205100	0.22008500	-0.00005400
		C	0.33233400	1.29555900	0.00001100

		C	1.69973000	1.05269400	0.00003600
		C	2.16335000	-0.25836100	-0.00002300
		H	1.64677500	-2.34809600	0.00005300
		H	-0.80788100	-1.91431000	0.00013500
		H	-0.06491800	2.30432900	-0.00000400
		H	2.40011900	1.87891900	0.00006800
		H	3.23019100	-0.45082800	-0.00002500
		N	-1.93914700	0.57634200	-0.00001900
		O	-2.71818400	-0.34645200	0.00002100
nitrosobenzene	Chloroform	C	1.27001900	-1.33188700	-0.00000200
		C	-0.09380500	-1.09894200	0.00003200
		C	-0.55160700	0.22033800	-0.00002400
		C	0.33244500	1.29526600	0.00002700
		C	1.69991400	1.05237400	0.00000500
		C	2.16369900	-0.25846000	-0.00004800
		H	1.64673000	-2.34788200	0.00008200
		H	-0.80920200	-1.91226800	0.00018200
		H	-0.06599800	2.30358600	0.00002800
		H	2.40036300	1.87867000	0.00000800
		H	3.23060400	-0.45098600	-0.00007000
		N	-1.94135600	0.57658600	0.00004300
		O	-2.71712300	-0.34742000	-0.00005800
nitrosobenzene	benzene	C	1.27038200	-1.33142800	-0.00001000
		C	-0.09355900	-1.09813400	-0.00006300
		C	-0.55115200	0.22052600	-0.00008800
		C	0.33255000	1.29491600	-0.00001200
		C	1.70011300	1.05211400	0.00004400
		C	2.16413500	-0.25847200	0.00002700
		H	1.64690600	-2.34760800	0.00004300
		H	-0.81041100	-1.91030400	-0.00003900
		H	-0.06723200	2.30274300	0.00001200
		H	2.40059100	1.87851900	0.00009400
		H	3.23112400	-0.45097700	0.00007200
		N	-1.94379200	0.57683500	-0.00007900
		O	-2.71615600	-0.34841800	0.00012300
TS_B	Ethanol	C	1.34280100	-1.22480200	0.51587100

		C	0.98740800	-0.24079700	1.43117500
		C	1.48772500	1.06914600	1.25551000
		C	2.42066400	1.31190100	0.29661300
		H	0.90522300	-2.21071400	0.62507600
		H	0.16865600	-0.41488800	2.11894200
		H	1.01092100	1.89384900	1.77432400
		H	2.68187600	2.33671300	0.05188100
		O	0.85950800	0.45146200	-1.44837900
		N	0.26739300	-0.50860900	-0.92374300
		C	-1.08327400	-0.20275100	-0.46532600
		C	-1.89514600	-1.27883000	-0.11947900
		C	-1.57811500	1.09495800	-0.45231400
		C	-3.20834500	-1.04985800	0.26648200
		H	-1.49264100	-2.28557500	-0.15339500
		C	-2.89392000	1.31746100	-0.06279600
		H	-0.92553300	1.90815800	-0.74497700
		C	-3.70985600	0.24981300	0.29939100
		H	-3.84422400	-1.88504700	0.53743800
		H	-3.28546300	2.32856700	-0.04369800
		H	-4.73637100	0.42765800	0.59917200
		C	3.28702200	0.23484700	-0.28406800
		H	3.50286300	0.47414000	-1.32646900
		H	4.24827700	0.28069100	0.24209100
		C	2.68792700	-1.18578000	-0.16464900
		H	2.59523500	-1.65232800	-1.14789800
		H	3.35402700	-1.82450700	0.42228200
TS_B	Chloroform	C	1.34366200	-1.22826800	0.50993200
		C	0.98732800	-0.25202400	1.43371600
		C	1.48019500	1.06094900	1.26254800
		C	2.40733000	1.31295700	0.30016700
		H	0.90952200	-2.21645800	0.61309400
		H	0.16971500	-0.43285200	2.12108200
		H	0.99910000	1.88089500	1.78498700
		H	2.65977000	2.33998400	0.05593900
		O	0.86371100	0.45563900	-1.44218500
		N	0.27090900	-0.50607900	-0.92427900

		C	-1.08048900	-0.20234600	-0.46639700
		C	-1.89256700	-1.27868700	-0.12277400
		C	-1.57495300	1.09515800	-0.45224200
		C	-3.20538700	-1.05011600	0.26388700
		H	-1.49029800	-2.28539700	-0.16071700
		C	-2.89051900	1.31722900	-0.06228700
		H	-0.92179800	1.90729200	-0.74654100
		C	-3.70637300	0.24953400	0.29898000
		H	-3.84195200	-1.88554200	0.53265400
		H	-3.28238200	2.32823400	-0.04319800
		H	-4.73299700	0.42713300	0.59861100
		C	3.28157400	0.24301000	-0.28271300
		H	3.49744700	0.48701500	-1.32392100
		H	4.24105200	0.29116600	0.24665900
		C	2.68885300	-1.18112400	-0.17068300
		H	2.59684600	-1.64169700	-1.15680200
		H	3.35800400	-1.81995600	0.41278300
TS_B	benzene	C	1.34459500	-1.23140000	0.50463500
		C	0.98773400	-0.26226100	1.43609600
		C	1.47406700	1.05332000	1.26912100
		C	2.39569200	1.31371100	0.30349000
		H	0.91346100	-2.22154400	0.60240500
		H	0.17146800	-0.44926700	2.12338100
		H	0.98958500	1.86889300	1.79529100
		H	2.64048200	2.34271600	0.06014900
		O	0.86732100	0.45971200	-1.43628100
		N	0.27393200	-0.50356500	-0.92465300
		C	-1.07809900	-0.20180300	-0.46721300
		C	-1.89033100	-1.27845400	-0.12577500
		C	-1.57234600	1.09549600	-0.45197200
		C	-3.20288300	-1.05042000	0.26132200
		H	-1.48811900	-2.28506400	-0.16718900
		C	-2.88775500	1.31697000	-0.06173400
		H	-0.91876700	1.90683800	-0.74755700
		C	-3.70349300	0.24914000	0.29847600
		H	-3.83995600	-1.88612600	0.52812800

		H	-3.27994700	2.32785700	-0.04234800
		H	-4.73019900	0.42642500	0.59805500
		C	3.27653800	0.25026600	-0.28216400
		H	3.49150800	0.49863800	-1.32248300
		H	4.23485800	0.30039800	0.24928000
		C	2.68960900	-1.17697100	-0.17644600
		H	2.59786300	-1.63224500	-1.16505800
		H	3.36169700	-1.81581000	0.40374900
furan	Acetonitrile	C	-0.00000100	-0.34712400	1.09032500
		C	-0.00000100	0.95461500	0.71714400
		C	-0.00000100	0.95461500	-0.71714400
		C	-0.00000100	-0.34712400	-1.09032500
		O	0.00006500	-1.15246900	0.00000000
		H	-0.00018600	-0.84430200	2.04608200
		H	-0.00006700	1.80923200	1.37503500
		H	-0.00006700	1.80923200	-1.37503500
		H	-0.00018600	-0.84430200	-2.04608200
Maleic anhydride	Acetonitrile	C	-1.12138100	-0.15534900	-0.00012900
		C	1.12141600	-0.15530500	-0.00018400
		C	0.66372200	1.25908900	-0.00010900
		C	-0.66378200	1.25910500	-0.00002400
		H	1.35178400	2.09076500	0.00038000
		H	-1.35214800	2.09051700	0.00028800
		O	-2.22057800	-0.60841200	0.00020500
		O	2.22061400	-0.60835200	0.00023800
		O	0.00002800	-0.96155100	-0.00019100
TS_C	Acetonitrile	C	-0.08773000	1.63308700	1.07117600
		C	1.23561100	1.30358900	0.68454300
		C	1.23561100	1.30358900	-0.68454300
		C	-0.08773000	1.63308700	-1.07117600
		O	-0.72781900	2.16778800	0.00000000
		H	-0.44403700	1.94815800	2.04002500
		H	2.02488600	0.99784800	1.35357000
		H	2.02488600	0.99784800	-1.35357000
		H	-0.44403700	1.94815800	-2.04002500
		C	-0.11075600	-1.25667800	1.13064800

C	-1.05711700	-0.21240200	0.70188500
C	-1.05711700	-0.21240200	-0.70188500
C	-0.11075600	-1.25667800	-1.13064800
H	-1.90675300	0.01478400	1.32830700
H	-1.90675300	0.01478400	-1.32830700
O	0.16288600	-1.67257900	2.21656600
O	0.16288600	-1.67257900	-2.21656600
O	0.51351200	-1.76422100	0.00000000

Table S2 Rate coefficients for 12 reactions in various solvents based on the proposed method and the IGT technique.

solute	solvent	Temp [K]	k_{TST} [dm^3 mol^{-1} s^{-1}]	$v^{\ddagger}$ [cm^{-1}]	scaled $v^{\ddagger}$ [cm^{-1}]	κ_{wigner}	k'_{TST_wigner} [dm^3 mol^{-1} s^{-1}]
This work							
TS_A	Ethanol	313	3.9×10^{-5}	-413.23	-392.57	1.14	4.5×10^{-5}
TS_A	THF	313	3.8×10^{-5}	-415.96	-395.16	1.14	4.4×10^{-5}
TS_A	Toluene	313	4.8×10^{-5}	-415.14	-394.38	1.14	5.6×10^{-5}
TS_A	cyclohexane	313	3.8×10^{-5}	-415.37	-394.60	1.14	4.4×10^{-5}
TS_A	cyclohexane	333	2.1×10^{-4}	-415.37	-394.60	1.12	2.4×10^{-4}
TS_A	cyclohexane	353	9.9×10^{-4}	-415.37	-394.60	1.11	1.1×10^{-3}
TS_A	cyclohexane	373	3.9×10^{-3}	-415.37	-394.60	1.10	4.4×10^{-3}
TS_A	cyclohexane	393	1.4×10^{-2}	-415.37	-394.60	1.09	1.5×10^{-2}
TS_B	Ethanol	298	1.5×10^{-1}	-387.72	-368.33	1.13	1.7×10^{-1}
TS_B	Chloroform	298	3.9×10^{-1}	-387.56	-368.18	1.13	4.4×10^{-1}
TS_B	Benzene	298	2.0×10^{-1}	-387.23	-367.87	1.13	2.3×10^{-1}
TS_C	Acetonitrile	300	7.4×10^{-4}	-542.07	-514.97	1.25	9.0×10^{-4}
IGT							
TS_A	Ethanol	313	2.1×10^{-7}	-413.23	-392.57	1.14	2.4×10^{-7}
TS_A	THF	313	2.1×10^{-7}	-415.96	-395.16	1.14	2.5×10^{-7}
TS_A	Toluene	313	2.6×10^{-7}	-415.14	-394.38	1.14	3.0×10^{-7}
TS_A	cyclohexane	313	2.4×10^{-7}	-415.37	-394.60	1.14	2.8×10^{-7}
TS_A	cyclohexane	333	1.4×10^{-6}	-415.37	-394.60	1.12	1.5×10^{-6}
TS_A	cyclohexane	353	6.4×10^{-6}	-415.37	-394.60	1.11	7.1×10^{-6}
TS_A	cyclohexane	373	2.6×10^{-5}	-415.37	-394.60	1.10	2.8×10^{-5}
TS_A	cyclohexane	393	8.9×10^{-5}	-415.37	-394.60	1.09	9.8×10^{-5}
TS_B	Ethanol	298	1.5×10^{-4}	-387.72	-368.33	1.13	1.8×10^{-4}
TS_B	Chloroform	298	4.0×10^{-4}	-387.56	-368.18	1.13	4.6×10^{-4}
TS_B	Benzene	298	2.1×10^{-4}	-387.23	-367.87	1.13	2.4×10^{-4}
TS_C	Acetonitrile	300	3.3×10^{-6}	-542.07	-514.97	1.25	4.2×10^{-6}

Table S3. Various parameters incorporated in the proposed translational model. All values were obtained using the QM/PCM technique.

	solvent	q_{elec}	Molecular weight [g mol^{-1}]	V_{cav} [×10^{-30} m^3]	V_{mol} [×10^{-30} m^3]	V_{free} [×10^{-31} m^3]
Reaction A						
cyclopentadiene	Ethanol	1	66.04695	142.362	98.978	2.12
TS_A	Ethanol	1	132.0939	247.281	183.772	2.07
cyclopentadiene	THF	1	66.04695	142.362	98.978	2.12
TS_A	THF	1	132.0939	247.281	183.772	2.07
cyclopentadiene	Toluene	1	66.04695	142.352	98.958	2.12
TS_A	Toluene	1	132.0939	247.257	183.749	2.07
cyclopentadiene	cyclohexane	1	66.04695	142.349	98.955	2.11
TS_A	cyclohexane	1	132.0939	247.254	183.745	2.06
Reaction B						
cyclohexadiene	Ethanol	1	80.0626	168.541	119.565	2.13
nitrosobenzene	Ethanol	1	107.0371	186.126	129.604	2.73
TS_B	Ethanol	1	187.0997	320.045	236.312	2.85
cyclohexadiene	Chloroform	1	80.0626	168.522	119.56	2.13
nitrosobenzene	Chloroform	1	107.0371	186.103	129.588	2.73
TS_B	Chloroform	1	187.0997	319.827	236.178	2.84
cyclohexadiene	Benzene	1	80.0626	168.541	119.565	2.13
nitrosobenzene	Benzene	1	107.0371	186.126	129.604	2.73
TS_B	Benzene	1	187.0997	320.045	236.312	2.85
Reaction C						
Furan	Acetonitrile	1	68.0626	128.952	87.803	2.24
maleic anhydride	Acetonitrile	1	98.00039	149.254	101.3	2.66
TS_C	Acetonitrile	1	166.0266	241.627	174.132	2.67

Table S4. Various parameters incorporated in the proposed rotational model. All values were obtained using the QM/PCM technique.

solute	Solvent	n_{iso}	σ	Θ_A	Θ_B	Θ_C	μ	μ_p	α
			[−]	[K]	[K]	[K]	[debye]	[debye]	[au]
Reaction A									
cyclopentadiene	Ethanol	1	2	0.40801	0.39717	0.20656	0.68650842	0.50780615	69.503215
TS_A	Ethanol	2	1	0.11572	0.0641	0.06102	0.9069	0.6011	169.8194
cyclopentadiene	THF	1	2	0.40801	0.39717	0.20656	0.6552015	0.50650119	67.092076
TS_A	THF	2	1	0.11572	0.0641	0.06102	0.8467	0.5998	161.10106
cyclopentadiene	Toluene	1	2	0.40823	0.39706	0.20661	0.58590069	0.50460063	61.626987
TS_A	Toluene	2	1	0.11569	0.06412	0.06104	0.7246	0.5971	142.70915
cyclopentadiene	cyclohexane	1	2	0.40828	0.39706	0.20662	0.572	0.50420063	60.52128
TS_A	cyclohexane	2	1	0.11568	0.06412	0.06104	0.7016	0.5966	139.178
Reaction B									
cyclohexadiene	Ethanol	1	2	0.2444	0.24397	0.1297	0.70360001	0.51570001	86.459554
nitrosobenzene	Ethanol	1	1	0.25379	0.07941	0.06048	4.8877462	3.8847496	104.42713
TS_B	Ethanol	2	1	0.08087	0.0229	0.02146	2.7798714	1.9490375	215.81045
cyclohexadiene	Chloroform	1	2	0.24446	0.24408	0.12978	0.6472	0.5136	81.046054
nitrosobenzene	Chloroform	1	1	0.25392	0.07939	0.06048	4.5971422	3.8597695	97.269821
TS_B	Chloroform	2	1	0.08089	0.02295	0.02151	2.479473	1.9308477	198.49242
cyclohexadiene	Benzene	1	2	0.2444	0.24397	0.1297	0.593	0.512	75.828096
nitrosobenzene	Benzene	1	1	0.25379	0.07941	0.06048	4.2950925	3.833294	90.320644
TS_B	Benzene	2	1	0.08087	0.0229	0.02146	2.2265998	1.914492	182.67083
Reaction C									
Furan	Acetnitril	1	2	0.45656	0.44925	0.22644	0.84630021	0.70460018	56.037154
maleinic anhydrid	Acetnitril	1	2	0.32824	0.11996	0.08785	5.3485	4.4905	63.461829
TS_C	Acetnitril	2	1	0.06979	0.0526	0.03901	6.4735856	5.2332258	130.17828

Table S5 Various parameters incorporated in the proposed configurational model. All values were obtained using the QM/PCM technique.

	solvent	concentration [mol dm^{-3}]	V_{cavity} ×10^{-30} [m^3]	N_{cell} ×10^{24}	N_{solute} ×10^{23}
Reaction A					
Cyclopentadiene	Ethanol	1	142.362	7.02	6.02
TS_A	Ethanol	1	247.281	4.04	6.02
cyclopentadiene	THF	1	142.362	7.02	6.02
TS_A	THF	1	247.281	4.04	6.02
cyclopentadiene	Toluene	1	142.352	7.02	6.02
TS_A	Toluene	1	247.257	4.04	6.02
cyclopentadiene	cyclohexane	1	142.349	7.02	6.02
TS_A	cyclohexane	1	247.254	4.04	6.02
Reaction B					
cyclohexadiene	Ethanol	1	168.541	5.93	6.02
nitrosobenzene	Ethanol	1	186.126	5.37	6.02
TS_B	Ethanol	1	320.045	3.12	6.02
cyclohexadiene	Chloroform	1	168.522	5.93	6.02
nitrosobenzene	Chloroform	1	186.103	5.37	6.02
TS_B	Chloroform	1	319.827	3.13	6.02
cyclohexadiene	Benzene	1	168.541	5.93	6.02
nitrosobenzene	Benzene	1	186.126	5.37	6.02
TS_B	Benzene	1	320.045	3.12	6.02
Reaction C					
furan	Acetonitrile	1	128.952	7.75	6.02
maleic anhydride	Acetonitrile	1	149.254	6.7	6.02
TS_C	Acetonitrile	1	241.627	4.14	6.02

Table S6. Total entropies and respective entropic terms for all solutes at a concentration of 1 mol dm^{-3} based on our proposed model (J mol^{-1} K^{-1}).

solute	solvent	T [K]	S_{elec}	S_{trans}	S_{rot}	S_{vib}	S_{cd}	S_{config}	S_{tot_calc}
cyclopentadiene	Ethanol	313	0	52.1	97.2	19.8	0	28.4	197.5
TS_A	Ethanol	313	0	60.6	126.6	85.7	0	23.5	296.4
cyclopentadiene	THF	313	0	52.2	97.2	19.8	0	28.4	197.6
TS_A	THF	313	0	60.6	126.7	85.0	0	23.5	295.7
cyclopentadiene	Toluene	313	0	52.1	97.2	19.9	0	28.4	197.6
TS_A	Toluene	313	0	60.6	126.6	87.6	0	23.5	298.3
cyclopentadiene	cyclohexane	313	0	52.2	97.2	19.9	0	28.4	197.6
TS_A	cyclohexane	313	0	60.6	126.7	84.9	0	23.5	295.7
cyclopentadiene	cyclohexane	333	0	52.9	98.0	23.0	0	28.4	202.4
TS_A	cyclohexane	333	0	61.4	127.4	93.4	0	23.5	305.7
cyclopentadiene	cyclohexane	353	0	52.9	98.0	23.0	0	28.4	202.4
TS_A	cyclohexane	353	0	61.4	127.4	93.4	0	23.5	305.7
cyclopentadiene	cyclohexane	373	0	54.3	99.4	29.8	0	28.4	211.9
TS_A	cyclohexane	373	0	62.8	128.9	110.8	0	23.5	326.0
cyclopentadiene	cyclohexane	393	0	55.0	100.1	33.3	0	28.4	216.8
TS_A	cyclohexane	393	0	63.4	129.5	119.8	0	23.5	336.2
cyclohexadiene	Ethanol	298	0	54.0	102.6	33.2	0	26.9	216.8
nitrosobenzene	Ethanol	298	0	59.7	101.8	51.9	0	26.0	239.3
TS_B	Ethanol	298	0	67.0	132.9	145.6	0	21.1	366.6
cyclohexadiene	Chloroform	298	0	54.0	102.7	33.2	0	26.9	216.8
nitrosobenzene	Chloroform	298	0	59.7	104.2	51.9	0	26.0	241.8
TS_B	Chloroform	298	0	67.0	134.6	145.0	0	21.1	367.7
cyclohexadiene	Benzene	298	0	54.0	102.7	33.2	0	26.9	216.8
nitrosobenzene	Benzene	298	0	59.7	104.2	51.9	0	26.0	241.8
TS_B	Benzene	298	0	67.0	135.7	144.1	0	21.1	367.9
furan	Acetonitrile	300	0	52.5	95.2	11.2	0	29.2	188.1
maleic anhydride	Acetonitrile	300	0	58.4	88.2	34.9	0	28.0	209.5
TS_C	Acetonitrile	300	0	65.1	108.5	98.5	0	23.7	295.8

Table S7. Total entropies and respective entropic terms for all solutes at a concentration of 1 mol dm^{-3} based on IGT (J mol^{-1} K^{-1}).

solute	solvent	T [K]	S_{elec}	S_{trans}	S_{rot}	S_{vib}	S_{cd}	S_{config}	S_{tot_calc}
cyclopentadiene	Ethanol	313	0	135.0	97.3	19.8	0	0	252.1
TS_A	Ethanol	313	0	143.7	126.7	85.7	0	0	356.1
cyclopentadiene	THF	313	0	135.0	97.3	19.8	0	0	252.1
TS_A	THF	313	0	143.7	126.7	85.0	0	0	355.3
cyclopentadiene	Toluene	313	0	135.0	97.3	19.9	0	0	252.2
TS_A	Toluene	313	0	143.7	126.7	87.6	0	0	357.9
cyclopentadiene	cyclohexane	313	0	135.0	97.3	19.9	0	0	252.2
TS_A	cyclohexane	313	0	143.7	126.7	84.9	0	0	355.3
cyclopentadiene	cyclohexane	333	0	135.8	98.0	23.0	0	0	256.9
TS_A	cyclohexane	333	0	144.5	127.4	93.4	0	0	365.3
cyclopentadiene	cyclohexane	353	0	136.5	98.8	26.4	0	0	261.7
TS_A	cyclohexane	353	0	145.2	128.2	102.0	0	0	375.4
cyclopentadiene	cyclohexane	373	0	137.2	99.4	29.8	0	0	266.5
TS_A	cyclohexane	373	0	145.9	128.9	110.8	0	0	385.6
cyclopentadiene	cyclohexane	393	0	137.9	100.1	33.3	0	0	271.3
TS_A	cyclohexane	393	0	146.5	129.5	119.8	0	0	395.8
cyclohexadiene	Ethanol	298	0	136.8	102.7	33.2	0	0	272.8
nitrosobenzene	Ethanol	298	0	140.4	116.2	51.9	0	0	308.5
TS_B	Ethanol	298	0	147.4	136.2	145.6	0	0	429.2
cyclohexadiene	Chloroform	298	0	136.8	102.7	33.2	0	0	272.8
nitrosobenzene	Chloroform	298	0	140.4	116.2	51.9	0	0	308.5
TS_B	Chloroform	298	0	147.4	136.2	145.0	0	0	428.6
cyclohexadiene	Benzene	298	0	136.8	102.7	33.2	0	0	272.8
nitrosobenzene	Benzene	298	0	140.4	116.2	51.9	0	0	308.5
TS_B	Benzene	298	0	147.4	136.2	144.1	0	0	427.7
furan	Acetonitrile	300	0	134.9	95.4	11.2	0	0	241.5
maleic anhydride	Acetonitrile	300	0	139.4	106.2	34.9	0	0	280.5
TS_C	Acetonitrile	300	0	146.0	125.2	98.5	0	0	369.7

Table S8 Electric and ZPE energies terms for all reactants, products, and TSs investigated in this study.

solute	solvent	E_{elec} [kJ mol^{-1}]	E_{ZPE} [kJ mol^{-1}]	f_{ZPE} [-]	E_0 [kJ mol^{-1}]
cyclopentadiene	Ethanol		243.9	0.975	
TS_A	Ethanol		496.4	0.975	
cyclopentadiene	THF		243.9	0.975	
TS_A	THF		496.3	0.975	
cyclopentadiene	Toluene		244.1	0.975	
TS_A	Toluene		496.9	0.975	
cyclopentadiene	cyclohexane		244.1	0.975	
TS_A	cyclohexane		496.9	0.975	
cyclohexadiene	Ethanol		322.7	0.975	
nitrosobenzene	Ethanol		256.9	0.975	
TS_B	Ethanol		586.5	0.975	
cyclohexadiene	Chloroform		322.9	0.975	
nitrosobenzene	Chloroform		256.9	0.975	
TS_B	Chloroform		586.9	0.975	
cyclohexadiene	Benzene		322.9	0.975	
nitrosobenzene	Benzene		256.9	0.975	
TS_B	Benzene		586.9	0.975	
furan	Acetonitrile		184.9	0.975	
maleic anhydride	Acetonitrile		147.6	0.975	
TS_C	Acetonitrile		338.3	0.975	

Table S9 Total energies and respective energetic terms for all reactants, products, and TSs based on our proposed method (kJ mol^{-1}).

solute	solvent	Temp	E_{elec}	E_{trans}	E_{rot}	E_{vib}	PV	H
cyclopentadiene	Ethanol	313	-509306.2	3.9	4.6	242.3	0	-509293.2
TS_A	Ethanol	313	-1019022.7	3.9	4.5	500.3	0	-1018514.0
cyclopentadiene	THF	313	-509545.6	3.9	4.2	242.5	0	-509294.8
TS_A	THF	313	-1019025.3	3.9	4.2	500.7	0	-1018516.7
cyclopentadiene	Toluene	313	-509306.1	3.9	4.4	242.4	0	-509293.0
TS_A	Toluene	313	-1019023.5	3.9	4.4	500.3	0	-1018514.8
cyclopentadiene	cyclohexane	313	-509543.6	3.9	4.2	242.6	0	-509293.0
TS_A	cyclohexane	313	-1019022.6	3.9	4.1	500.7	0	-1018513.9
cyclopentadiene	cyclohexane	333	-509543.6	4.2	4.4	243.6	0	-509291.5
TS_A	cyclohexane	333	-1019022.6	4.2	4.4	503.5	0	-1018510.7
cyclopentadiene	cyclohexane	353	-509543.6	4.4	4.7	244.7	0	-509289.9
TS_A	cyclohexane	353	-1019022.6	4.4	4.6	506.4	0	-1018507.2
cyclopentadiene	cyclohexane	373	-509543.6	4.7	4.9	246.0	0	-509288.1
TS_A	cyclohexane	373	-1019022.6	4.7	4.9	509.6	0	-1018503.5
cyclopentadiene	cyclohexane	393	-509543.6	4.9	5.2	247.3	0	-509286.2
TS_A	cyclohexane	393	-1019022.6	4.9	5.1	513.0	0	-1018499.6
cyclohexadiene	Ethanol	298	-612756.5	3.7	4.3	321.3	0	-612427.2
nitrosobenzene	Ethanol	298	-949054.5	3.7	6.2	260.0	0	-948784.7
TS_B	Ethanol	298	-1561766.1	3.7	5.9	595.6	0	-1561160.8
cyclohexadiene	Chloroform	298	-612750.0	3.7	4.1	321.4	0	-612420.8
nitrosobenzene	Chloroform	298	-949046.0	3.7	6.2	260.0	0	-948776.2
TS_B	Chloroform	298	-1561753.8	3.7	5.5	595.8	0	-1561148.7
cyclohexadiene	Benzene	298	-612756.1	3.7	4.0	321.5	0	-612426.9
nitrosobenzene	Benzene	298	-949050.9	3.7	6.2	260.0	0	-948781.0
TS_B	Benzene	298	-1561762.8	3.7	4.9	595.9	0	-1561157.6
furan	Acetonitrile	300	-603822.2	3.7	4.5	183.0	0	-603631.0
maleic anhydride	Acetonitrile	300	-995668.1	3.7	6.2	150.6	0	-995507.5
TS_C	Acetonitrile	300	-1599432.3	3.7	6.2	346.7	0	-1599075.70

Table S10 Total energies and respective energetic terms for all reactants, products, and TSs based on IGT (kJ mol^{-1}).

solute	solvent	Temp	E_{elec}	E_{trans}	E_{rot}	E_{vib}	PV	H
cyclopentadiene	Ethanol	313	-509306.2	3.9	3.9	242.3	2.6	-509291.2
TS_A	Ethanol	313	-1019022.7	3.9	3.9	500.3	2.6	-1018512.0
cyclopentadiene	THF	313	-509545.6	3.9	3.9	242.5	2.6	-509292.8
TS_A	THF	313	-1019025.3	3.9	3.9	500.7	2.6	-1018514.6
cyclopentadiene	Toluene	313	-509306.1	3.9	3.9	242.4	2.6	-509291.1
TS_A	Toluene	313	-1019023.5	3.9	3.9	500.3	2.6	-1018512.5
cyclopentadiene	cyclohexane	313	-509543.6	3.9	3.9	242.6	2.6	-509290.7
TS_A	cyclohexane	313	-1019022.6	3.9	3.9	500.7	2.6	-1018511.5
cyclopentadiene	cyclohexane	333	-509543.6	4.2	4.2	243.6	2.8	-509289.0
TS_A	cyclohexane	333	-1019022.6	4.2	4.2	503.5	2.8	-1018508.1
cyclopentadiene	cyclohexane	353	-509543.6	4.4	4.4	244.7	2.9	-509287.2
TS_A	cyclohexane	353	-1019022.6	4.4	4.4	506.4	2.9	-1018504.5
cyclopentadiene	cyclohexane	373	-509543.6	4.7	4.7	246.0	3.1	-509285.3
TS_A	cyclohexane	373	-1019022.6	4.7	4.7	509.6	3.1	-1018500.6
cyclopentadiene	cyclohexane	393	-509543.6	4.9	4.9	247.3	3.3	-509283.2
TS_A	cyclohexane	393	-1019022.6	4.9	4.9	513.0	3.3	-1018496.5
cyclohexadiene	Ethanol	298	-612756.5	3.7	3.7	321.3	2.5	-612425.3
nitrosobenzene	Ethanol	298	-949054.5	3.7	3.7	260.0	2.5	-948784.7
TS_B	Ethanol	298	-1561766.1	3.7	3.7	595.6	2.5	-1561160.5
cyclohexadiene	Chloroform	298	-612750.0	3.7	3.7	321.4	2.5	-612418.8
nitrosobenzene	Chloroform	298	-949046.0	3.7	3.7	260.0	2.5	-948776.2
TS_B	Chloroform	298	-1561753.8	3.7	3.7	595.8	2.5	-1561148.1
cyclohexadiene	Benzene	298	-612756.1	3.7	3.7	321.4	2.5	-612424.9
nitrosobenzene	Benzene	298	-949050.9	3.7	3.7	260.0	2.5	-948781.0
TS_B	Benzene	298	-1561762.8	3.7	3.7	595.8	2.5	-1561157.3
furan	Acetonitrile	300	-603822.2	3.7	3.7	183.0	2.5	-603629.3
maleic anhydride	Acetonitrile	300	-995668.1	3.7	3.7	150.6	2.5	-995507.5
TS_C	Acetonitrile	300	-1599432.3	3.7	3.7	346.7	2.5	-1599075.7

Appendix 1. A model of the restricted rotation of a dipole in an electrostatic field.

A rotational term was modeled based on the restricted rotation of a dipole in an electrostatic field as depicted in the figure below.
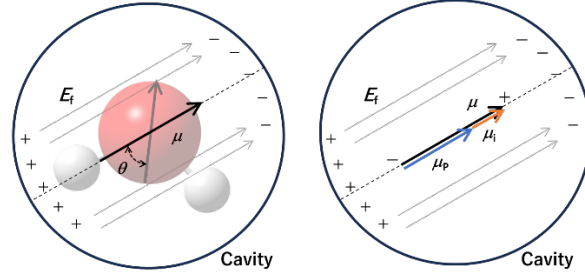

Fig. 2 Diagram summarizing the restricted rotation of a dipole (μ) in an electrostatic field (E_f).

The orientation of a rigid rotor can be specified using the Euler angles θ, ϕ and ψ, which have ranges of 0 to π, 0 to 2π, and 0 to 2π, respectively. The rotational Hamiltonian for the kinetic energy of such a rotor can be written in terms of these angles and their conjugate momenta (p_θ, p_ϕ and p_ψ). Assuming that the dipole moment lies along the molecule-fixed z-axis and the external electric field is collinear, neither ψ nor ϕ will be included in the Hamiltonian. In this case, the electrostatic restriction on rotation will be along the angle θ and the Hamiltonian for a linear, non-linear and polar molecule having dipole moment μ in an electric field (E_f) can be represented as

$$\mathcal{H}_{\text{rot.,linear}} = \frac{1}{2I}\left(p_\theta^2 + \frac{1}{\sin^2\theta}p_\varphi^2\right) + \mu E_{\text{f}}(1 - \cos\theta) \tag{A1.1}$$

and

$$\mathcal{H}_{\text{rot.,non-linear}} = \frac{\sin^2\psi}{2I_a}\left(p_\theta - \frac{\cos\psi}{\sin\theta\sin\psi}\left(p_\phi - \cos\theta\, p_\psi\right)\right)^2$$

$$+ \frac{\cos^2\psi}{2I_b}\left(p_\theta - \frac{\cos\psi}{\sin\theta\sin\psi}\left(p_\phi - \cos\theta\, p_\psi\right)\right)^2 + \frac{1}{2I_c}p_\psi{}^2 + \mu E_{\text{f}}(1 - \cos\theta) \tag{A1.2}$$

The last term in both Eqs. (A1) and (A2) represents the potential energy associated with the molecular dipole in the electric field. In the case that the Hamiltonian is defined, we can obtain classical partition functions based on the integrals

$$q_{\text{rot.,linear}} = \frac{1}{\sigma}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_0^\pi\int_0^{2\pi}\frac{1}{h^2}e^{-\mathcal{H}_{rot}(p,q)/k_BT}\,\mathrm{d}p_\theta\,\mathrm{d}p_\phi\,\mathrm{d}\theta\,\mathrm{d}\phi \tag{A1.3}$$

and

$$q_{\text{rot,non linear}} =$$
$$\frac{1}{\sigma}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_0^\pi\int_0^{2\pi}\int_0^{2\pi}\frac{1}{h^3}e^{-\mathcal{H}_{rot}(p,q)/k_BT}\,\mathrm{d}p_\theta\,\mathrm{d}p_\phi\,\mathrm{d}p_\psi\,\mathrm{d}\theta\,\mathrm{d}\phi\,\mathrm{d}\psi \tag{A1.4}$$

These integrals can be used to calculate q_{rot} as

$$q_{\text{rot.,linear}} = \frac{1}{\sigma} \frac{k_B T}{2hc\bar{B}} \frac{k_B T}{2\mu E} \left[1 - \exp(-\frac{2\mu E_f}{k_B T}) \right] \tag{A1.5}$$

and

$$q_{\text{rot,non linear}} = \frac{1}{\sigma} \left(\frac{k_B T}{hc} \right)^{\frac{3}{2}} \left(\frac{\pi}{\bar{A}\bar{B}\bar{C}} \right)^{\frac{1}{2}} \frac{k_B T}{2\mu E} \left[1 - \exp(-\frac{2\mu E_f}{k_B T}) \right] \tag{A1.6}$$

Based on statistical thermodynamics, the rotational entropy ($S_{\text{rot.}}$) is calculated as

$$S_{\text{rot.}} = \frac{d}{dT} (-RT \ln q_{\text{rot.}}) \tag{A1.7}$$

The entropy value can then be obtained according to the equations

$$S_{\text{rot,linear}} =$$

$$R[\ln \left\{ \frac{1}{\sigma} \frac{k_B T}{2hc\bar{B}X} [1 - \exp(-X)] \right\} - \frac{X \exp(-X)}{[1 - \exp(-X)]} + 2] \tag{A1.8}$$

and

$$S_{\text{rot,non-linear}} =$$

$$R[\ln \left\{ \frac{1}{\sigma} \left(\frac{k_B T}{hc} \right)^{\frac{3}{2}} \left(\frac{\pi}{\bar{A}\bar{B}\bar{C}} \right)^{\frac{1}{2}} \frac{1}{X} [1 - \exp(-X)] \right\} - \frac{X \exp(-X)}{[1 - \exp(-X)]} + \frac{5}{2}] \tag{A1.9}$$

Where

$$X = \frac{2\mu E_f}{k_B T} \tag{A1.10}$$

A molecule with a polarizability of P has an induced dipole moment μ_i, by the surrounding electric field E_f, according to:

$$E = \frac{\mu_i}{\alpha} \tag{A1.11}$$

μ_i is estimated by the difference between μ and the permanent dipole moment (the dipole moment without a cavity), μ_p:

$$\mu_i = \mu - \mu_p \tag{A1.12}$$

Appendix 2. Specific procedure to calculate thermodynamic data using Gaussian program.

Sample input file for nitrosobenzene.

% chk=sample.chk
#p opt freq wb97xd/6-311++g(d,p) scrf=(solvent=ethanol,read)

Title Card Required

0 1

C	1.26978100	-1.33231400	-0.00001700
C	-0.09394100	-1.09979600	0.00000300
C	-0.55205100	0.22008500	-0.00005400
C	0.33233400	1.29555900	0.00001100
C	1.69973000	1.05269400	0.00003600
C	2.16335000	-0.25836100	-0.00002300
H	1.64677500	-2.34809600	0.00005300
H	-0.80788100	-1.91431000	0.00013500
H	-0.06491800	2.30432900	-0.00000400
H	2.40011900	1.87891900	0.00006800
H	3.23019100	-0.45082800	-0.00002500
N	-1.93914700	0.57634200	-0.00001900
O	-2.71818400	-0.34645200	0.00002100

alpha=1.2

--Link1--
% chk=sample.chk
#p wb97xd/6-311++g(d,p) scrf=(solvent=ch3oh,read)
geom=allcheck guess=(read,only)

alpha=1.0

--Link1--

% chk=sample.chk

wb97xd/6-311++g(d,p) geom=allcheck guess=read

---

*The route section "#p" is required to display the cavity size in the results.

1. Geometric optimization and a frequency analysis were conducted using PCMs with van der Waals radii (employing UFF in the case of this sample) scaled by $\alpha = 1.2$ (as opposed to the default value of 1.1 in Gaussian 16). The results provided the molecular weight, m, $V_{\alpha=1.2}$, the dipole-moment, μ, rotational constants ($\tilde{A}$, $\tilde{B}$, $\tilde{C}$) (or rotational temperatures Θ_A, Θ_B, Θ_C) and the polarizability, P. It was considered that any molecular orbital and density functional theory method could be employed with PCMs and that the frequency scaling factor was preferably obtained in advance.

```
---------------------
- Thermochemistry -
---------------------
Temperature   298.150 Kelvin.   Pressure    1.00000 Atm.
Atom     1 has atomic number   6 and mass  12.00000
Atom     2 has atomic number   6 and mass  12.00000
Atom     3 has atomic number   6 and mass  12.00000
Atom     4 has atomic number   6 and mass  12.00000
Atom     5 has atomic number   6 and mass  12.00000
Atom     6 has atomic number   6 and mass  12.00000
Atom     7 has atomic number   1 and mass   1.00783
Atom     8 has atomic number   1 and mass   1.00783
Atom     9 has atomic number   1 and mass   1.00783
Atom    10 has atomic number   1 and mass   1.00783
Atom    11 has atomic number   1 and mass   1.00783
Atom    12 has atomic number   7 and mass  14.00307
Atom    13 has atomic number   8 and mass  15.99491
Molecular mass:    107.03711 amu.
Principal axes and moments of inertia in atomic units:
                         1          2          3
     Eigenvalues --  341.28183 1090.75538 1432.03721
          X             1.00000    0.00265    0.00000
          Y            -0.00265    1.00000   -0.00000
          Z            -0.00000    0.00000    1.00000
This molecule is an asymmetric top.
Rotational symmetry number  1.
Rotational temperatures (Kelvin)     0.25379    0.07941    0.06048 ←    Θ_A, Θ_B, Θ_C
Rotational constants (GHZ):          5.28813    1.65458    1.26026
Zero-point vibrational energy    256909.3 (Joules/Mol)
                                     61.40279 (Kcal/Mol)
Warning -- explicit consideration of   6 degrees of freedom as
         vibrations may cause significant error
Vibrational temperatures:     150.32    360.03    372.02    604.45    655.86
           (Kelvin)           680.32    902.03    987.07    989.14   1123.04
                             1219.25   1252.67   1399.23   1467.13   1470.08
                             1490.83   1499.88   1586.55   1650.41   1710.15
                             1743.99   1926.90   1957.38   2154.41   2175.30
                             2330.24   2398.16   2425.95   4601.41   4613.98
                             4622.09   4636.15   4641.77
```

```
Force inversion solution in PCM.↓
----------------------------------------------------------------
Polarizable Continuum Model (PCM)↓
================================↓
Model                : PCM.↓
Atomic radii         : UFF (Universal Force Field).↓
Polarization charges : Total charges.↓
Charge compensation  : None.↓
Solution method      : Matrix inversion.↓
Cavity type          : Scaled VdW (van der Waals Surface) (Alpha=1.200).↓
Cavity algorithm     : GePol (No added spheres)↓
                       Default sphere list used, NSphG=   13.↓
                       Lebedev-Laikov grids with approx.   5.0 points / Ang**2
                       Smoothing algorithm: York/Karplus (Gamma=1.0000).↓
                       Polarization charges: spherical gaussians, with↓
                                             point-specific exponents (IZeta=
).↓
                       Self-potential: point-specific (ISelfS= 7).↓
                       Self-field    : sphere-specific E.n sum rule (ISelfD=
.↓
 1st derivatives     : Analytical E(r).r(x)/FMM algorithm (CHGder, D1EAlg=3).
                       Cavity 1st derivative terms included.↓
 2nd derivatives     : Analytical E(r).r(xy)/FMM algorithm (CHGder, D2EAlg=3)
                       Cavity 2nd derivative terms included.↓
Solvent              : Ethanol, Eps=  24.852000 Eps(inf)=   1.852593↓
----------------------------------------------------------------
Spheres list:↓
ISph  on  Nord   ReO   Alpha     Xe          Ye          Ze↓
   1   C    1   1.9255  1.200    1.269781   -1.332314   -0.000017↓
   2   C    2   1.9255  1.200   -0.093941   -1.099796    0.000003↓
   3   C    3   1.9255  1.200   -0.552051    0.220085   -0.000054↓
   4   C    4   1.9255  1.200    0.332334    1.295559    0.000011↓
   5   C    5   1.9255  1.200    1.699730    1.052694    0.000036↓
   6   C    6   1.9255  1.200    2.163350   -0.258361   -0.000023↓
   7   H    7   1.4430  1.200    1.646775   -2.348096    0.000053↓
   8   H    8   1.4430  1.200   -0.807881   -1.914310    0.000135↓
   9   H    9   1.4430  1.200   -0.064918    2.304329   -0.000004↓
  10   H   10   1.4430  1.200    2.400119    1.878919    0.000068↓
  11   H   11   1.4430  1.200    3.230191   -0.450828   -0.000025↓
  12   N   12   1.8300  1.200   -1.939147    0.576342   -0.000019↓
  13   O   13   1.7500  1.200   -2.718184   -0.346452    0.000021↓
----------------------------------------------------------------
GePol: Number of generator spheres         =        13↓
GePol: Total number of spheres             =        13↓
GePol: Number of exposed spheres           =        13 (100.00%)↓
GePol: Number of points                    =      1458↓
GePol: Average weight of points            =      0.12↓
GePol: Minimum weight of points            =   0.13D-07↓
GePol: Maximum weight of points            =   0.21541↓
GePol: Number of points with low weight    =        75↓
GePol: Fraction of low-weight points (<1% of avg) =  5.14%↓
GePol: Cavity surface area                 =   177.703 Ang**2↓
GePol: Cavity volume                       =   186.126 Ang**3↓  ⟶ V_cav = V_f=1.2
Leave Link  301 at Wed Sep 27 12:37:08 2023, MaxMem=  5368709120 cpu:
      0.5 elap:        0.1↓
```

$V_{cav} = V_{f=1.2}$

```
charge                  0.0000 electrons.
Dipole moment (field-independent basis, Debye):↓
   X=        4.8745   Y=        -0.3596   Z=        0.0002  Tot=        4.8877↓   ⟶ μ
Quadrupole moment (field-independent basis, Debye-Ang):↓
  XX=      -50.0176   YY=       -40.2756   ZZ=      -48.1979↓
  XY=        0.7053   XZ=         0.0001   YZ=       -0.0003↓
Traceless Quadrupole moment (field-independent basis, Debye-Ang):↓
  XX=       -3.8539   YY=         5.8881   ZZ=       -2.0342↓
  XY=        0.7053   XZ=         0.0001   YZ=       -0.0003↓
Octapole moment (field-independent basis, Debye-Ang**2):↓
 XXX=       41.5171  YYY=        -3.2038  ZZZ=        0.0004  XYY=        5.8825↓
 XXY=       -1.7638  XXZ=         0.0000  XZZ=       -8.9925  YZZ=       -0.2752↓
 YYZ=        0.0013  XYZ=         0.0002↓
Hexadecapole moment (field-independent basis, Debye-Ang**3):↓
XXXX=     -824.9688 YYYY=      -278.4906 ZZZZ=      -52.7045 XXXY=        2.4737↓
XXXZ=        0.0013 YYYX=         8.3037 YYYZ=       -0.0022 ZZZX=       -0.0002↓
ZZZY=       -0.0005 XXYY=      -176.9718 XXZZ=     -144.6596 YYZZ=      -67.6702↓
XXYZ=        0.0002 YYXZ=         0.0005 ZZXY=        1.1951↓
N-N= 3.253139460066D+02 E-N=-1.493554951516D+03  KE= 3.601605192425D+02↓
   Exact polarizability: 150.042    3.518  108.715    0.000    0.000   54.525↓  ⟶ Avg. α = 104.42
  Approx polarizability: 125.640    5.965   99.300   -0.000    0.000   50.880↓
```

Avg. α = 104.42

2. A single point calculation was conducted using PCMs for the structure optimized in step (1) with the same van der Waals radii scaled by α = 1.0. The result provided $V_{\alpha=1.0}$ after which the free volume, V_{free}, could be calculated as

$$v_{\text{free}} = \left(V_{a=1.2}^{1/3} - V_{a=1.0}^{1/3} \right)^3.$$

```
---------------------------------------------------------------------------↓
Polarizable Continuum Model (PCM)↓
================================↓
Model                  : PCM. ↓
Atomic radii           : UFF (Universal Force Field).↓
Polarization charges   : Total charges.↓
Charge compensation    : None.↓
Solution method        : On-the-fly selection.↓
Cavity type            : VdW (van der Waals Surface) (Alpha=1.000).↓
Cavity algorithm       : GePol (No added spheres)↓
                         Default sphere list used, NSphG=    13.↓
                         Lebedev-Laikov grids with approx.   5.0 points / Ang**2.↓
                         Smoothing algorithm: York/Karplus (Gamma=1.0000).↓
                         Polarization charges: spherical gaussians, with↓
                                          point-specific exponents (IZeta= 3).↓
                         Self-potential: point-specific (ISelfS= 7).↓
                         Self-field    : sphere-specific E.n sum rule (ISelfD= 2).↓
Solvent                : Ethanol, Eps=  24.852000 Eps(inf)=   1.852593↓
---------------------------------------------------------------------------↓
Spheres list:↓
ISph  on   Nord    ReO    Alpha      Xe          Ye          Ze↓
   1   C     1    1.9255  1.000    1.269781    -1.332314   -0.000017↓
   2   C     2    1.9255  1.000   -0.093941    -1.099796    0.000003↓
   3   C     3    1.9255  1.000   -0.552051     0.220085   -0.000054↓
   4   C     4    1.9255  1.000    0.332334     1.295559    0.000011↓
   5   C     5    1.9255  1.000    1.699730     1.052694    0.000036↓
   6   C     6    1.9255  1.000    2.163350    -0.258361   -0.000023↓
   7   H     7    1.4430  1.000    1.646775    -2.348096    0.000053↓
   8   H     8    1.4430  1.000   -0.807881    -1.914310    0.000135↓
   9   H     9    1.4430  1.000   -0.064918     2.304329   -0.000004↓
  10   H    10    1.4430  1.000    2.400119     1.878919    0.000068↓
  11   H    11    1.4430  1.000    3.230191    -0.450828   -0.000025↓
  12   N    12    1.8300  1.000   -1.939147     0.576342   -0.000019↓
  13   O    13    1.7500  1.000   -2.718184    -0.346452    0.000021↓
---------------------------------------------------------------------------↓
GePol: Number of generator spheres              =       13↓
GePol: Total number of spheres                  =       13↓
GePol: Number of exposed spheres                =       13 (100.00%)↓
GePol: Number of points                         =     1208↓
GePol: Average weight of points                 =        0.12↓
GePol: Minimum weight of points                 =    0.16D-08↓
GePol: Maximum weight of points                 =    0.22001↓
GePol: Number of points with low weight         =       63↓
GePol: Fraction of low-weight points (<1% of avg) =     5.22%↓
GePol: Cavity surface area                      =  146.528 Ang**2↓
GePol: Cavity volume                            =  129.604 Ang**3↓
```
$\longrightarrow V_{mol} = V_{f=1.0}$

The translational entropy, q_{trans}, $S_{trans.}$, was calculated using the corrected Sackur-Tetrode equation, written as

$$q_{\text{trans}} = \left(v_{\text{free}} \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3}{2}} \right)$$

$$E_{\text{trans}} = \frac{3}{2} RT$$

$$S_{\text{trans}} = R \left[\ln \left(v_{\text{free}} \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3}{2}} \right) + \frac{3}{2} \right].$$

Taking nitrosobenzene in ethanol as an example, these calculations become

$$v_{\text{free}} = \left(V_{a=1.2}^{1/3} - V_{a=1.0}^{1/3}\right)^3 = (186.126^{1/3} - 129.604^{1/3})^3 \times 10^{-30} = 2.73243 \times 10^{-31}$$

and

$$q_{\text{trans}} = \left(v_{\text{free}}\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}}\right)$$

$$= 2.73243 \times 10^{-31}\left(\frac{2\pi \times \dfrac{107.03711}{6.02 \times 10^{-23} \times 1000} \times 1.38 \times 10^{-23} \times 298.15}{(6.63 \times 10^{-34})^2}\right)^{\frac{3}{2}}$$

$$E_{\text{trans}} = \frac{3}{2}RT$$

$$S_{\text{trans}} = 8.314\left[\ln\left(2.73243 \times 10^{-31}\left(\frac{2\pi \times \dfrac{107.03711}{6.02 \times 10^{-23} \times 1000} \times 1.38 \times 10^{-23} \times 298.15}{(6.63 \times 10^{-34})^2}\right)^{\frac{3}{2}}\right) + \frac{3}{2}\right]$$

$$= 59.7 \; [\text{J mol}^{-1} \text{ K}^{-1}].$$

3. A single-point calculation was conducted for the same structure without PCMs and the result provided the dipole moment in a vacuum, μ_p. The induced dipole moment, μ_i, and surrounding electric field, E_f, were then calculated using the equations

$$\mu_i = \mu - \mu_p$$

and

$$E_f = \frac{\mu_i}{\alpha}.$$

```
Electronic spatial extent (au):  <R**2>=        886.9356↓
Charge=               -0.0000 electrons↓
Dipole moment (field-independent basis, Debye):↓
    X=           3.8726   Y=          -0.3070   Z=          0.0001  Tot=          3.8847↓    ← μp
Quadrupole moment (field-independent basis, Debye-Ang):↓
    XX=         -49.7889   YY=         -40.9166   ZZ=        -48.1775↓
    XY=           0.7319   XZ=           0.0001   YZ=         -0.0003↓
Traceless Quadrupole moment (field-independent basis, Debye-Ang):↓
    XX=          -3.4945   YY=           5.3777   ZZ=         -1.8832↓
    XY=           0.7319   XZ=           0.0001   YZ=         -0.0003↓
Octapole moment (field-independent basis, Debye-Ang**2):↓
    XXX=          31.9799   YYY=          -2.8379   ZZZ=         0.0003   XYY=          4.0208↓
    XXY=          -1.6894   XXZ=          -0.0000   XZZ=        -9.5958   YZZ=         -0.2392↓
    YYZ=           0.0012   XYZ=           0.0002↓
Hexadecapole moment (field-independent basis, Debye-Ang**3):↓
    XXXX=        -821.5646   YYYY=        -284.1445   ZZZZ=       -52.6920   XXXY=         3.0021↓
    XXXZ=           0.0011   YYYX=           8.2003   YYYZ=        -0.0021   ZZZX=        -0.0003↓
    ZZZY=          -0.0005   XXYY=        -178.9262   XXZZ=      -144.5464   YYZZ=       -67.9195↓
    XXYZ=           0.0002   YYXZ=           0.0004   ZZXY=         1.2157↓
N-N= 3.253139460066D+02 E-N=-1.493460102213D+03  KE= 3.601574999949D+02↓
1¥1¥GINC-GAUSSIAN¥SP¥RwB97XD¥6-311++G(d,p)¥C6H5N1O1¥IZATO¥27-Sep-2023¥↓
O¥¥# wb97xd/6-311++g(d,p) geom=allcheck guess=read¥¥Title Card Require↓
```

In the case of nitrosobenzene, these calculations are

$$\mu_i = \mu - \mu_p = (4.8877[\text{debye}] - 3.8847\,[\text{debye}]) \times 3.33564 \times 10^{-30} = 3.346 \times 10^{-31}[\text{C m}]$$

and

$$E_f = \frac{\mu_i}{\alpha} = \frac{3.346 \times 10^{-31}[\text{C m}]}{104.42713 \times 1.65 \times 10^{-41}[\text{C}^2\ \text{m}^2\ \text{J}^{-1}]} = 1.94 \times 10^9\ [\text{J m}^{-1}\ \text{C}^{-1}].$$

Units

Units in GaussView	SI
Dipole moment: 1 [Debye]	3.33564 x 10^{-30} [C m]
Polarizability: 1 [au]	1.648777 x 10^{-41} [C^2 m^2 J^{-1}]

The rotational entropy, $S_{rot.}$, could be calculated by inserting the values obtained according to the procedures noted above along with the relevant constants into the equations

$$q_{\text{rot,linear}} = \frac{1}{\sigma} \frac{T}{\Theta_B} \frac{1}{X} \{1 - \exp(-X)\}$$

$$E_{\text{rot,linear}} = RT \left\{ 2 - \frac{X \exp(-X)}{1-\exp(-X)} \right\}$$

$$S_{\text{rot,linear}} = R \left[\ln \left\{ \frac{1}{\sigma} \frac{k_B T}{2hc\tilde{B}} \frac{1-\exp(-X)}{X} \right\} - \frac{X \exp(-X)}{1-\exp(-X)} + 2 \right]$$

$$= R \left[\ln \left\{ \frac{1}{\sigma} \frac{T}{\Theta_B} \frac{1-\exp(-X)}{X} \right\} - \frac{X \exp(-X)}{1-\exp(-X)} + 2 \right]$$

and

$$q_{\text{rot,non linear}} = \frac{n_{iso}\sqrt{\pi}}{\sigma} \left(\frac{T^3}{\Theta_A \Theta_B \Theta_C} \right)^{\frac{1}{2}} \frac{1-\exp(-X)}{X}$$

$$E_{\text{rot,non linear}} = RT \left(\frac{5}{2} - \frac{X \exp(-X)}{1-\exp(-X)} \right)$$

$$S_{\text{rot, non-linear}} = R \left[\ln \left\{ \frac{n_{iso}}{\sigma} \left(\frac{k_B T}{hc} \right)^{\frac{3}{2}} \left(\frac{\pi}{\tilde{A}\tilde{B}\tilde{C}} \right)^{\frac{1}{2}} \frac{1-\exp(-X)}{X} \right\} - \frac{X \exp(-X)}{1-\exp(-X)} + \frac{5}{2} \right]$$

$$= R \left[\ln \left\{ \frac{n_{iso}\sqrt{\pi}}{\sigma} \left(\frac{T^3}{\Theta_A \Theta_B \Theta_C} \right)^{\frac{1}{2}} \frac{1-\exp(-X)}{X} \right\} - \frac{X \exp(-X)}{1-\exp(-X)} + \frac{5}{2} \right]$$

Taking nitrosobenzen as an example, these calculations are

$$\Theta_A = 0.25379 \ [K]$$
$$\Theta_B = 0.07941 \ [K]$$
$$\Theta_C = 0.06048 \ [K]$$
$$X = \frac{2\mu E}{k_B T} = \frac{2 \times 4.89 \times 3.33564 \times 10^{-30} \times 1.94 \times 10^9}{1.381 \times 10^{-23} \times 298} = 15.40 \ [-]$$

and

$$q_{\text{rot,non-linear}} =$$

$$\frac{3.14^{0.5}}{2} \left(\frac{298.15^3}{0.25379 \times 0.07941 \times 0.06048} \right)^{0.5} = 101.8 \ [\text{J K}^{-1} \text{ mol}^{-1}].$$

$$E_{\text{rot,non-linear}} =$$

$$8.314 \times 298.15 \times \left(\frac{5}{2} - \frac{15.40 \exp(-15.40)}{[1-\exp(-15.40)]} \right)$$

$$= 6.197 \ [\text{kJ mol}^{-1}].$$

$S_{\text{rot,non-linear}} =$

$$8.314\left[\ln\left\{\frac{3.14^{0.5}}{2}\left(\frac{298.15^3}{0.25379\times0.07941\times0.06048}\right)^{0.5}\frac{1-\exp(-15.40)}{15.40}\right\} - \frac{15.40\exp(-15.40)}{1-\exp(-15.40)} + \frac{5}{2}\right]$$

$$= 101.8 \text{ [J mol}^{-1}\text{ K}^{-1}\text{]}.$$

4. The vibrational terms without scaling parameters could be obtained from the thermochemistry output file.

In the case of nitrosobenzene in ethanol, this file was as follows.

$$q_{vib} = 9.23499$$

$$E_{zpe} = 0.097852 \times 2625.506 \text{ [kJ mol}^{-1}] = 256.9 \text{ [kJ mol}^{-1}]$$

$$E_{vib} = 63.51 \text{ [kcal mol}^{-1}] = 265.7 \text{ [kJ mol}^{-1}]$$

$$S_{vib} = 11.489 \text{ [cal mol}^{-1} \text{ K}^{-1}] = 48.1 \text{ [J mol}^{-1} \text{ K}^{-1}]$$

```
Zero-point correction=                        0.097852 (Hartree/Particl  ◄─── E_ZPE
Thermal correction to Energy=                 0.104044↓
Thermal correction to Enthalpy=               0.104988↓
Thermal correction to Gibbs Free Energy=      0.067368↓
Sum of electronic and zero-point Energies=  -361.411237↓
Sum of electronic and thermal Energies=     -361.405045↓
Sum of electronic and thermal Enthalpies=   -361.404100↓
Sum of electronic and thermal Free Energies= -361.441720↓
↓
                    E (Thermal)        CV              S↓
                    KCal/Mol      Cal/Mol-Kelvin  Cal/Mol-Kelvin↓
Total               65.289          23.235          79.178↓
Electronic           0.000           0.000           0.000↓
Translational        0.889           2.981          39.921↓
Rotational           0.889           2.981          27.769↓
Vibrational         63.511   ◄─ E_vib  17.274        11.489↓  ◄─── S_vib
Vibration     1      0.605           1.946           3.369↓
Vibration     2      0.663           1.762           1.729↓
Vibration     3      0.667           1.748           1.671↓
Vibration     4      0.783           1.427           0.892↓
Vibration     5      0.814           1.348           0.778↓
Vibration     6      0.830           1.310           0.730↓
                 Q              Log10(Q)          Ln(Q)↓
Total Bot    0.103009D-30       -30.987126       -71.350494↓
Total V=0    0.105059D+15        14.021435        32.285548↓
Vib (Bot)    0.905473D-44       -44.043124      -101.413042↓
Vib (Bot)  1 0.196255D+01         0.292821         0.674245↓
Vib (Bot)  2 0.779879D+00        -0.107973        -0.248616↓
Vib (Bot)  3 0.751707D+00        -0.123951        -0.285408↓
Vib (Bot)  4 0.417918D+00        -0.378909        -0.872469↓
Vib (Bot)  5 0.374406D+00        -0.426657        -0.982414↓
Vib (Bot)  6 0.355865D+00        -0.448715        -1.033204↓
Vib (V=0)    0.923499D+01  ◄─ q_vib 0.965437       2.223000↓
Vib (V=0)  1 0.252524D+01         0.402303         0.926337↓
Vib (V=0)  2 0.142640D+01         0.154241         0.355152↓
Vib (V=0)  3 0.140281D+01         0.146998         0.338477↓
Vib (V=0)  4 0.115166D+01         0.061323         0.141201↓
Vib (V=0)  5 0.112464D+01         0.051015         0.117466↓
Vib (V=0)  6 0.111371D+01         0.046772         0.107697↓
Electronic   0.100000D+01         0.000000         0.000000↓
Translational 0.435267D+08        7.638755        17.588884↓
Rotational   0.261362D+06         5.417243        12.473663↓
↓
```

Applying f_{vib} and f_{zpe}, we can obtain scaled parameters.

$$q_{vib\ scaled} = 11.139$$

$$E_{zpe\ scaled} = 250.5 \text{ [kJ mol}^{-1}]$$

$$E_{vib\ scaled} = 63.51 \text{ [kcal mol}^{-1}] = 259.97 \text{ [kJ mol}^{-1}]$$

$$S_{vib\ scaled} = 51.87 \text{ [J mol}^{-1} \text{ K}^{-1}]$$

5. The configurational entropy at a concentration of C was calculated from V_{cav} and V_{solute}. As an example, for a solute at a concentration of 1 mol dm^{-3} in a solvent volume of 1 dm^3, we have the following.

$C = 1\ [\text{mol dm}^{-3}]$,

$V_{\text{solution}} = 1\ [\text{dm}^3]$,

$N_{\text{solute}} = C \cdot L \cdot V_{\text{solution}} = 1\ [\text{mol dm}^{-3}] \times 6.02 \times 10^{23}[\text{mol}^{-1}] \times 1\ [\text{dm}^3] = 6.02 \times 10^{23}$,

$N_{\text{cells}} = \dfrac{V_{\text{solution}}}{V_{\text{cav}}} = \dfrac{1 \times 10^{27}\ [\text{Å}^3]}{186.126[\text{Å}^3]} = 5.3727 \times 10^{24}$

and

$q_{\text{config}} \approx \exp\left\{\dfrac{N_{\text{cell}}}{N_{\text{solute}}} \ln \dfrac{N_{\text{cell}}}{N_{\text{solute}}} - \left(\dfrac{N_{\text{cell}}}{N_{\text{solute}}} - 1\right) \ln \left(\dfrac{N_{\text{cell}}}{N_{\text{solute}}} - 1\right)\right\}$

$= \exp\left\{\dfrac{5.37 \times 10^{23}}{6.02 \times 10^{23}} \ln \dfrac{5.37 \times 10^{23}}{6.02 \times 10^{23}} - \left(\dfrac{5.37 \times 10^{23}}{6.02 \times 10^{23}} - 1\right) \ln \left(\dfrac{5.37 \times 10^{23}}{6.02 \times 10^{23}} - 1\right)\right\} = 22.9\ [-]$

$E_{\text{config}} = 0\ [\text{kJ mol}^{-1}]$

$S_{\text{config}} = 8.314\ [\text{J mol}^{-1}\ \text{K}^{-1}] \times 22.9 = 26.0\ [\text{J mol}^{-1}\ \text{K}^{-1}]$

6. Finally, the entropic terms obtained as noted above are summed.

Using nitrosobenzene as an example, this summation would be

$H = U = E_{\text{elec}} + E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{config}}$

$= E_{\text{elec}} + 3.7 + 6.2 + 260.0 + 0 = E_{\text{elec}} + 269.9$

$S = S_{\text{elec}} + S_{\text{trans}} + S_{\text{rot}} + S_{\text{vib}} + S_{\text{config}}$

$= 0 + 59.7 + 101.8 + 51.9 + 26.0 = 239.3$

Appendix 3. Calculations S and G at temperature of 298.15 K and a concentration of 1 mol dm^{-3} based on IGT.

The partition function and entropy at 1 atm and 298.15 K can be written as:

$$q_{\text{trans\_IGT at 1 atm}} = V \left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}} = \frac{RT}{p} \left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}} = \frac{8.314 \times 298.15}{101300} \left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}},$$

$$S_{\text{trans\_IGT at 1 atm}} = R \left[\ln\left\{\frac{8.314 \times 298.15}{101300 \times N_A} \left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}}\right\} + \frac{5}{2}\right].$$

A pressure of 24.5 (24.47) atm in a volume of 1 dm^3 corresponds to a concentration of 1 mol dm^{-3} at 298.15 K based on the ideal gas equation of state.

$$q_{\text{trans\_IGT at 1 mol dm}^{-3}} = V \left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}} = \frac{8.314 \times 298.15}{24.47 \times 101300} \left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}} = 0.001 \left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}}$$

$$S_{\text{trans\_IGT at 1 mol dm}^{-3}} = R \left[\ln\left\{\frac{0.001}{N_A} \left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}}\right\} + \frac{5}{2}\right].$$

Consequently, the S and G corrections for converting the state at 1 atm to 1 mol dm^{-3} at 298.15 K can be calculated as -26.78 J mol^{-1} K^{-1} and +7.98 Jmol^{-1}.

$$\Delta S(1 \text{ atm} \rightarrow 1 \text{ mol dm}^3) = S_{\text{trans}_{\text{IGT}} \text{at 1 mol dm}^{-3}} - S_{\text{trans}_{\text{IGT}} \text{at 1 atm}}$$

$$= R \ln \frac{101300 \times 0.001}{8.314 \times 298.15} = -26.6 \text{ [J mol}^{-1} \text{ K}^{-1}\text{]}$$

$$\Delta G(1 \text{ atm} \rightarrow 1 \text{ mol dm}^3) = -T\Delta S(1 \text{ atm} \rightarrow 1 \text{ mol dm}^3) = -298.15 \times -26.58$$

$$= 7.93 \text{ [kJ mol}^{-1}\text{]}$$

Appendix 4. Derivation Eqn (21) from Eqn (22)

$$q_{\text{configuration}} = W^{\frac{1}{N_{\text{solute}}}} = \left(\frac{N_{\text{cell}}!}{N_{\text{solute}}!(N_{\text{cell}} - N_{\text{solute}})!}\right)^{\frac{1}{N_{\text{solute}}}}$$

$$\ln q_{\text{configuration}} = \frac{1}{N_{\text{solute}}} \ln\left(\frac{N_{\text{cell}}!}{N_{\text{solute}}!(N_{\text{cell}} - N_{\text{solute}})!}\right)$$

Applying the approximation ($N \ln N - N \approx \ln N!$) gives

$$\ln q_{\text{config}} = \frac{1}{N_{\text{solute}}} \ln[N_{\text{cell}}! - \{N_{\text{solute}}! + (N_{\text{cell}} - N_{\text{solute}})!\}]$$

$$= \frac{1}{N_{\text{solute}}}[N_{\text{cell}} \ln N_{\text{cell}} - N_{\text{cell}} - \{N_{\text{solute}} \ln N_{\text{solute}} - N_{\text{solute}} + (N_{\text{cell}} - N_{\text{solute}}) \ln(N_{\text{cell}} - N_{\text{solute}}) - (N_{\text{cell}} - N_{\text{solute}})\}]$$

$$= \frac{1}{N_{\text{solute}}}[N_{\text{cell}} \ln N_{\text{cell}} - \{N_{\text{solute}} \ln N_{\text{solute}} + (N_{\text{cell}} - N_{\text{solute}}) \ln(N_{\text{cell}} - N_{\text{solute}})\}]$$

$$= \frac{1}{N_{\text{solute}}}\left[N_{\text{cell}} \ln N_{\text{cell}} - \left\{N_{\text{solute}} \ln N_{\text{solute}} + N_{\text{solute}}\left(\frac{N_{\text{cell}}}{N_{\text{solute}}} - 1\right) \ln N_{\text{solute}}\left(\frac{N_{\text{cell}}}{N_{\text{solute}}} - 1\right)\right\}\right]$$

$$= \frac{1}{N_{\text{solute}}}\left[N_{\text{cell}} \ln N_{\text{cell}} - N_{\text{solute}} \ln N_{\text{solute}} - N_{\text{solute}}\left(\frac{N_{\text{cell}}}{N_{\text{solute}}} - 1\right) \ln N_{\text{solute}}\left(\frac{N_{\text{cell}}}{N_{\text{solute}}} - 1\right)\right]$$

$$= \frac{N_{\text{cell}}}{N_{\text{solute}}} \ln N_{\text{cell}} - \ln N_{\text{solute}} - \left(\frac{N_{\text{cell}}}{N_{\text{solute}}} - 1\right) \ln N_{\text{solute}}\left(\frac{N_{\text{cell}}}{N_{\text{solute}}} - 1\right)$$

$$= \frac{N_{\text{cell}}}{N_{\text{solute}}} \ln N_{\text{cell}} - \ln N_{\text{solute}} - \left(\frac{N_{\text{cell}}}{N_{\text{solute}}} - 1\right) \ln N_{\text{solute}} - \left(\frac{N_{\text{cell}}}{N_{\text{solute}}} - 1\right) \ln\left(\frac{N_{\text{cell}}}{N_{\text{solute}}} - 1\right)$$

$$= \frac{N_{\text{cell}}}{N_{\text{solute}}} \ln N_{\text{cell}} - \ln N_{\text{solute}} - \frac{N_{\text{cell}}}{N_{\text{solute}}} \ln N_{\text{solute}} + \ln N_{\text{solute}} - \left(\frac{N_{\text{cell}}}{N_{\text{solute}}} - 1\right) \ln\left(\frac{N_{\text{cell}}}{N_{\text{solute}}} - 1\right)$$

$$= \frac{N_{\text{cell}}}{N_{\text{solute}}} \ln N_{\text{cell}} - \frac{N_{\text{cell}}}{N_{\text{solute}}} \ln N_{\text{solute}} - \left(\frac{N_{\text{cell}}}{N_{\text{solute}}} - 1\right) \ln\left(\frac{N_{\text{cell}}}{N_{\text{solute}}} - 1\right)$$

$$= \frac{N_{\text{cell}}}{N_{\text{solute}}} \ln \frac{N_{\text{cell}}}{N_{\text{solute}}} - \left(\frac{N_{\text{cell}}}{N_{\text{solute}}} - 1\right) \ln\left(\frac{N_{\text{cell}}}{N_{\text{solute}}} - 1\right)$$

$$\ln q_{\text{config}} = \frac{N_{\text{cell}}}{N_{\text{solute}}} \ln \frac{N_{\text{cell}}}{N_{\text{solute}}} - \left(\frac{N_{\text{cell}}}{N_{\text{solute}}} - 1\right) \ln\left(\frac{N_{\text{cell}}}{N_{\text{solute}}} - 1\right)$$

$$\leftrightarrow q_{\text{config}} = \exp\left\{\frac{N_{\text{cell}}}{N_{\text{solute}}} \ln \frac{N_{\text{cell}}}{N_{\text{solute}}} - \left(\frac{N_{\text{cell}}}{N_{\text{solute}}} - 1\right) \ln\left(\frac{N_{\text{cell}}}{N_{\text{solute}}} - 1\right)\right\}$$

Appendix 5 Gibbs energy formalisms based on statistical thermodynamics for nonlocalized and localized system.

Based on statistical thermodynamics, the Gibbs energy at a temperature T can be defined in terms of a canonical partition function, Q, as:

$$G(T) = G(0\text{ K}) - k_B T \ln Q + PV. \qquad (A6.1)$$

The Q value for independent and indistinguishable molecules (that is, a nonlocalized system) is obtained from the molecular partition function as:

$$Q = \frac{1}{N!} q^N. \qquad (A6.2)$$

Substituting this relationship into Eq. (A6.1) gives:

$$G = G(0\text{ K}) - k_B T \ln \frac{1}{N!} q^N + PV. \qquad (A6.3)$$

Applying the Stirling's approximation to Eq. (A6.3) then provides:

$$
\begin{aligned}
G &= G(0\text{ K}) - k_B N T \ln q + k_B T \ln \frac{1}{N!} + PV \\
&= G(0\text{ K}) - k_B N T \ln q + k_B N T \ln N - k_B N T + PV \\
&= G(0\text{ K}) - n R T \ln q + n R T \ln N - n R T + n R T \\
&= G(0\text{ K}) - n R T \ln \frac{q}{N}. \qquad (A6.4)
\end{aligned}
$$

On this basis, the standard molar Gibbs energy ($G_m°$) can be defined in terms of a molar partition function at the standard state ($q°$) as:

$$G_m^\circ(T) = G_m(0\text{ K}) - RT \ln \frac{q^\circ}{L}. \qquad (A6.5)$$

Here, we consider a general chemical reaction:

$$a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}, \qquad (A6.6)$$

where A, B, C and D are the reactants or products of the reaction and a, b, c and d are the stoichiometric coefficients. In this case, the change in G for the reaction between reactants in their standard states at the same temperature ($\Delta_r G°$) will be:

$$\Delta_r G^\circ = c G_m^\circ(\text{C}, T) + d G_m^\circ(\text{D}, T) - \{a G_m^\circ(\text{A}, T) + b G_m^\circ(\text{B}, T)\}$$

$$= c G_m(\text{C}, 0\text{ K}) + d G_m(\text{D}, 0\text{ K}) - \{a G_m(\text{A}, 0\text{ K}) + b G_m(\text{B}, 0\text{ K})\} - RT \left\{ c \ln \frac{q_C^\circ}{L} + d \ln \frac{q_D^\circ}{L} - a \ln \frac{q_A^\circ}{L} - b \ln \frac{q_B^\circ}{L} \right\}$$

$$= \Delta_r G(0\ \text{K}) - RT\left\{c\ln\frac{q_C^\circ}{L} + d\ln\frac{q_D^\circ}{L} - a\ln\frac{q_A^\circ}{L} - b\ln\frac{q_B^\circ}{L}\right\}\ . \tag{A6.7}$$

Because $\Delta_r G(0\ \text{K})$ is equal to the potential energy, $\Delta_r E_0$, the above becomes:

$$\Delta_r G^\circ = \Delta_r E_0 - RT\left\{c\ln\frac{q_C^\circ}{L} + d\ln\frac{q_D^\circ}{L} - a\ln\frac{q_A^\circ}{L} - b\ln\frac{q_B^\circ}{L}\right\}$$

$$= \Delta_r E_0 - RT\ln\frac{\left(\frac{q_C^\circ}{L}\right)^c\left(\frac{q_D^\circ}{L}\right)^d}{\left(\frac{q_A^\circ}{L}\right)^a\left(\frac{q_B^\circ}{L}\right)^b}$$

$$\leftrightarrow \frac{\Delta_r G^\circ}{RT} = \frac{\Delta_r E_0}{RT} - \ln\frac{\left(\frac{q_C^\circ}{L}\right)^c\left(\frac{q_D^\circ}{L}\right)^d}{\left(\frac{q_A^\circ}{L}\right)^a\left(\frac{q_B^\circ}{L}\right)^b}\ . \tag{A6.8}$$

Taking the exponential of both sides, we obtain the relationship:

$$\frac{\left(\frac{q_C^\circ}{L}\right)^c\left(\frac{q_D^\circ}{L}\right)^d}{\left(\frac{q_A^\circ}{L}\right)^a\left(\frac{q_B^\circ}{L}\right)^b}\exp\left(-\frac{\Delta_r E_0}{RT}\right) = \exp\left(-\frac{\Delta_r G^\circ}{RT}\right). \tag{A6.9}$$

In contrast, Q for independent and distinguishable molecules (that is, a localized system) is obtained from the molecular partition function as:

$$Q = q^N\ . \tag{A6.10}$$

In the liquid phase, PV is assumed to be zero. On this basis, G_m° can be defined as:

$$G_m^\circ(T) = G_m^\circ(0\ \text{K}) - nRT\ln q^\circ\ . \tag{A6.11}$$

The change in Gibbs energy for the reaction in Eq. (A6.6), $\Delta_r G^\circ$, will then be:

$$\Delta_r G^\circ = cG_m(C, 0\ \text{K}) + dG_m(D, 0\ \text{K}) - \{aG_m(A, 0\ \text{K}) + bG_m(B, 0\ \text{K})\} - RT\{c\ln q_C^\circ + d\ln q_D^\circ - a\ln q_A^\circ - b\ln q_B^\circ\}$$

$$= \Delta_r E_0 - RT\ln\frac{(q_C^\circ)^c(q_D^\circ)^d}{(q_A^\circ)^a(q_B^\circ)^b}$$

$$\leftrightarrow -\frac{\Delta_r G^\circ}{RT} = -\frac{\Delta_r E_0}{RT} + \ln\frac{(q_C^\circ)^c(q_D^\circ)^d}{(q_A^\circ)^a(q_B^\circ)^b}\ . \tag{A6.12}$$

Taking the exponential of both sides gives:

$$\frac{(q_{\mathrm{C}}^{\circ})^{c}(q_{\mathrm{D}}^{\circ})^{d}}{(q_{\mathrm{A}}^{\circ})^{a}(q_{\mathrm{B}}^{\circ})^{b}} \exp\left(-\frac{\Delta_{\mathrm{r}}E_0}{RT}\right) = \exp\left(-\frac{\Delta_{\mathrm{r}}G^{\circ}}{RT}\right). \tag{A6.13}$$

Appendix 6 Effect of the choice of the standard state on kinetics in the IGT.

In the IGT model, regardless of the chosen standard state (whether it is 1 atm or 1 mol dm^{-3}), the same rate coefficient will be obtained if calculated consistently for that standard state. In the IGT model, the standard state is represented by defining the volume, so the partition function per unit volume is equal, regardless of the chosen standard state. As an example, in the case of calculations involving reaction A, the rate coefficients obtained from transition state theory are also equal, as shown blow.

$$k_{\text{TST}} = L \frac{k_{\text{B}}T}{h} \frac{\frac{\mathring{q}_{\text{TS}}}{V_{\text{TS}}}}{\frac{q_{\text{A}}}{V_{\text{A}}} \frac{\mathring{q}_{\text{B}}}{V_{\text{B}}}} \exp\left(-\frac{\Delta E_0^{\ddagger}}{RT}\right)$$

$$= 6.02 \times 10^{23}[\text{mol}^{-1}] \times \frac{1.3806\times10^{-23}[\text{m}^2 \text{ kg s}^{-2} \text{ K}^{-1}]\times313[\text{K}]}{6.626\times10^{-34}[\text{m}^2 \text{ kg s}^{-1}]} \times \frac{8.43\times10^{40}[\text{m}^{-3}]}{2.81\times10^{37}[\text{m}^{-3}]\cdot2.81\times10^{37}[\text{m}^{-3}]} \times$$

$$\exp\left(-\frac{58.432\times1000[\text{J mol}^{-1}]}{8.314[\text{m}^2 \text{ kg s}^{-2} \text{ K}^{-1}\text{mol}^{-1}]\times313[\text{K}]}\right)$$

$$= 7.4 \times 10^{-5} \text{ [dm}^3 \text{ mol}^{-1} \text{ s}^{-1}] \text{ or } [\text{L mol}^{-1} \text{ s}^{-1}]$$

$$k_{\text{TST,IGT at 1 mol dm}^{-3}} = \frac{k_{\text{B}}T}{hC^{\circ}} \exp\left(-\frac{\Delta G_{1\,\text{mol/L}}^{\ddagger\circ}}{RT}\right)$$

$$\Delta G_{1\,\text{mol/L}}^{\ddagger\circ} = 101.5387 \text{ [kJ mol}^{-1}]$$

$$k_{\text{TST,IGT at 1 mol dm}^{-3}} =$$

$$\frac{1.3806\times10^{-23}[\text{m}^2 \text{ kg s}^{-2} \text{ K}^{-1}]\times313[\text{K}]}{6.626\times10^{-34}[\text{m}^2 \text{ kg s}^{-1}]} \frac{1}{10^3[\text{mol m}^{-3}]} \exp\left(-\frac{101.5387\times1000[\text{J mol}^{-1}]}{8.314[\text{m}^2 \text{ kg s}^{-2} \text{ K}^{-1}\text{mol}^{-1}]\times313[\text{K}]}\right)$$

$$= 7.4 \times 10^{-5} \text{ [dm}^3 \text{ mol}^{-1} \text{ s}^{-1}] \text{ or } [\text{L mol}^{-1} \text{ s}^{-1}]$$

$$k_{\text{TST,IGT at 1 atm}} = \frac{k_{\text{B}}T}{hC^{\circ}} \exp\left(-\frac{\Delta G_{1\,\text{atm}}^{\ddagger\circ}}{RT}\right) = \frac{k_{\text{B}}T}{h} \frac{RT}{p} \exp\left(-\frac{\Delta G_{1\,\text{atm}}^{\ddagger\circ}}{RT}\right)$$

$$\Delta G_{1\,\text{atm}}^{\ddagger\circ} = 109.9863671 \text{ [kJ mol}^{-1}]$$

$$k_{\text{TST,IGT at 1 atm}} =$$

$$\frac{1.3806\times10^{-23}[\text{m}^2 \text{ kg s}^{-2} \text{ K}^{-1}]\times313[\text{K}]}{6.626\times10^{-34}[\text{m}^2 \text{ kg s}^{-1}]} \frac{8.314[\text{m}^2 \text{ kg s}^{-2} \text{ K}^{-1}\text{mol}^{-1}]\times313[\text{K}]}{101300 \text{ [Pa]}} \exp\left(-\frac{109.9863671\times1000[\text{J mol}^{-1}]}{8.314[\text{m}^2 \text{ kg s}^{-2} \text{ K}^{-1}\text{mol}^{-1}]\times313[\text{K}]}\right)$$

$$= 7.4 \times 10^{-5} \text{ [dm}^3 \text{ mol}^{-1} \text{ s}^{-1}] \text{ or } [\text{L mol}^{-1} \text{ s}^{-1}]$$

Appendix 7 The rate coefficient calculation ignoring *PV* based on the IGT.

In the IGT method, *PV* cannot be ignored when calculating the enthalpies of reactants A, B, and the activated complex TS. The rate coefficients calculated using the activation Gibbs energy without considering *PV* and those using partition function and potential energy difference, which should match, do not coincide.

In a unimolecular reaction, the number of molecules of reactants and the activated complex are equal, so whether or not *PV* is considered, its effect cancels out. However, in a bimolecular reaction, since there is one more reactant molecule than TS, if *PV* is not considered, the value of the activation Gibbs energy would increase by *RT* (= *PV*). We are concerned that the rate coefficients calculated using the activation Gibbs energy without considering *PV* (eqn (56)) and those using the partition function and the potential energy difference (eqn (54)), which should ideally give the same result, in fact do not. We believe that this discrepancy arises from not applying equivalent corrections to the partition function despite correcting for *RT* (= *PV*) when determining the enthalpy (and Gibbs energy). In this study, to prioritize consistency between eqs (54) and (56), we did not ignore the *PV* term in the IGT method. However, if the sole purpose is to determine the enthalpy or Gibbs energy, we believe it is reasonable to neglect *PV*.

Consider reaction A in ethanol.

$$k_{\text{TST\_IGT}} = \frac{k_{\text{B}}T}{h} L \frac{\frac{q^{\circ}_{\text{IGT,TS}}}{V^{\circ}}}{\frac{q^{\circ}_{\text{IGT,A}}}{V^{\circ}} \frac{q^{\circ}_{\text{IGT,B}}}{V^{\circ}}} \exp\left(-\frac{\Delta E_0^{\ddagger}}{RT}\right) \tag{54}$$

$$k_{\text{TST IGT}} = \frac{1.3806 \times 10^{-23}[\text{m}^2\,\text{kg}\,\text{s}^{-2}\,\text{K}^{-1}] \times 313.15[\text{K}]}{6.626 \times 10^{-34}[\text{m}^2\,\text{kg}\,\text{s}^{-1}]} \times 6.02 \times 10^{23}$$

$$\frac{8.43 \times 10^{40}[\text{m}^{-3}]}{2.82 \times 10^{37}[\text{m}^{-3}] \cdot 2.82 \times 10^{37}[\text{m}^{-3}]} \times \exp\left(-\frac{73.7386 \times 1000[\text{J mol}^{-1}]}{8.314[\text{m}^2\,\text{kg}\,\text{s}^{-2}\,\text{K}^{-1}\text{mol}^{-1}] \times 313.15[\text{K}]}\right)$$

$$= 2.09 \times 10^{-10}\ [\text{m}^3\,\text{s}^{-1}\,\text{mol}^{-1}]$$
$$= 2.1 \times 10^{-7}\ [\text{dm}^3\ \text{mol}^{-1}\,\text{s}^{-1}]\text{ or }[\text{L mol}^{-1}\,\text{s}^{-1}]$$

$$k_{\text{TST\_IGT}} = \frac{k_{\text{B}}T}{hC^{\circ}} \exp\left(-\frac{\Delta G_{1\,\text{mol/L}}^{\ddagger\circ}}{RT}\right) \tag{56}$$

$$k_{\text{TST IGT}} = \frac{1.3806 \times 10^{-23}[\text{m}^2\,\text{kg}\,\text{s}^{-2}\,\text{K}^{-1}] \times 313.15[\text{K}]}{6.626 \times 10^{-34}[\text{m}^2\,\text{kg}\,\text{s}^{-1}]} \frac{1}{10^3[\text{mol m}^{-3}]} \exp\left(-\frac{116.87 \times 1000[\text{J mol}^{-1}]}{8.314[\text{m}^2\,\text{kg}\,\text{s}^{-2}\,\text{K}^{-1}\text{mol}^{-1}] \times 313.15[\text{K}]}\right)$$

$$= 2.09 \times 10^{-10}\ [\text{m}^3\,\text{s}^{-1}\,\text{mol}^{-1}]$$
$$= 2.1 \times 10^{-7}\ [\text{dm}^3\ \text{mol}^{-1}\,\text{s}^{-1}]\text{ or }[\text{L mol}^{-1}\,\text{s}^{-1}]$$

$$k_{\text{TST IGT}} = \frac{k_{\mathrm{B}}T}{hC^{\circ}} \exp\left(-\frac{\Delta G^{\ddagger\circ}_{1\,\text{mol/L,IGT,PV}=0}}{RT}\right)$$

$$= \frac{1.3806\times10^{-23}\left[\text{m}^2\text{ kg s}^{-2}\text{ K}^{-1}\right]\times313[\text{K}]}{6.626\times10^{-34}[\text{m}^2\text{ kg s}^{-1}]} \frac{1}{10^3\left[\text{mol m}^{-3}\right]} \exp\left(-\frac{116.87\times1000+2602.282[\text{J mol}^{-1}]}{8.314\left[\text{m}^2\text{ kg s}^{-2}\text{ K}^{-1}\text{mol}^{-1}\right]\times313[\text{K}]}\right)$$

$$= 7.7\times10^{-8}\ [\text{dm}^3\ \text{mol}^{-1}\text{ s}^{-1}]\ \text{or}\ [\text{L}\ \text{mol}^{-1}\text{ s}^{-1}]$$

Here, $\Delta G_{1\text{mol/L,IGT,PV}=0}$ represents the activation Gibbs energy calculated by the IGT method with *PV* set to zero. In the case of a bimolecular reaction, there is a relationship between the Gibbs energy considering *PV* ($\Delta G_{1\text{mol/L,IGT,PV}\neq0}$) and the following.

$$\Delta G^{\ddagger\circ}_{1\,\text{mol/L,IGT,PV}=0} = \Delta G^{\ddagger\circ}_{1\,\text{mol/L,IGT,PV}\neq0} + RT$$

It is evident from the above that the rate coefficients calculated using the two processes, which should be equivalent, do not agree. I attribute this discrepancy to the fact that the IGT method formulates the partition function on the basis of an ideal gas compressed to a volume of 1 dm^3. Despite this, the gas is treated as ideal, leading to inaccurate results when calculating activation Gibbs energies and rate coefficients in accordance with statistical thermodynamics without considering *PV*. Of course, for the purpose of determining the enthalpy or Gibbs energy of the solute, *PV* can be considered negligible.

The aim of the present study was to formulate the partition function for the solute and derive rate coefficients from this function. To ensure coherence between the rate coefficients derived from the partition function and those obtained from the activation Gibbs energy, we have opted not to ignore *PV*, even within the IGT method.

Recognizing potential reader interest in how the rate coefficient changes when w_{PV} is disregarded in the calculation of activation Gibbs energy, we have shown values of $k_{\text{TST,IGT}}$ ignoring w_{PV} in following table and figure. This approach provided worse predictions compared to the normal IGT.

TABLE. The activation enthalpies, activation entropies, activation Gibbs energies and rate coefficients for 12 reactions in various solvents based on the IGT technique (note that w_{PV} work has been ignored in calculations of H).

| reaction	solvent	Temp. [K]	$\Delta H^{\ddagger}$ [kJ mol^{-1}]	$\Delta S^{\ddagger}$ [J mol^{-1} K^{-1}]	$\Delta G^{\ddagger}$ [kJ mol^{-1}]	$k_{TST,PV=0}$ [dm^3 mol^{-1} s^{-1}]	k'_{TST_wigner} [dm^3 mol^{-1} s^{-1}]	k_{exp} [dm^3 mol^{-1} s^{-1}]
A	Ethanol	313	73.1	-148.2	119.5	7.7×10^{-8}	8.9×10^{-8}	4.6×10^{-6} [a]
A	THF	313	73.6	-148.2	119.4	7.9×10^{-8}	9.1×10^{-8}	2.5×10^{-6} [a]
A	Toluene	313	72.3	-149.0	118.9	9.6×10^{-8}	1.1×10^{-7}	4.0×10^{-6} [a]
A	cyclohexane	313	72.4	-149.0	119.1	8.8×10^{-8}	1.0×10^{-7}	4.5×10^{-6} [b]
A	cyclohexane	333	72.6	-148.5	122.1	5.0×10^{-7}	5.7×10^{-7}	2.3×10^{-5} [b]
A	cyclohexane	353	72.8	-147.9	125.5	2.3×10^{-6}	2.6×10^{-6}	9.7×10^{-5} [b]
A	cyclohexane	373	73.0	-147.4	128.0	9.4×10^{-6}	1.0×10^{-5}	3.5×10^{-4} [b]
A	cyclohexane	393	73.2	-146.8	131.0	3.3×10^{-5}	3.6×10^{-5}	1.1×10^{-3} [b]
B	Ethanol	298	51.9	-152.5	97.2	5.7×10^{-5}	6.5×10^{-5}	1.2×10^{-2} [c]
B	Chloroform	298	49.3	-152.7	94.8	1.5×10^{-4}	17×10^{-4}	1.1×10^{-2} [c]
B	benzene	298	50.9	-153.5	96.5	7.6×10^{-5}	8.7×10^{-5}	1.0×10^{-2} [c]
C	acetonitrile	300	63.5	-152.3	107.5	1.2×10^{-6}	1.5×10^{-6}	1.8×10^{-5} [d]

[a] ref 25 [b] ref 26 [c] ref 27 [d] ref 28
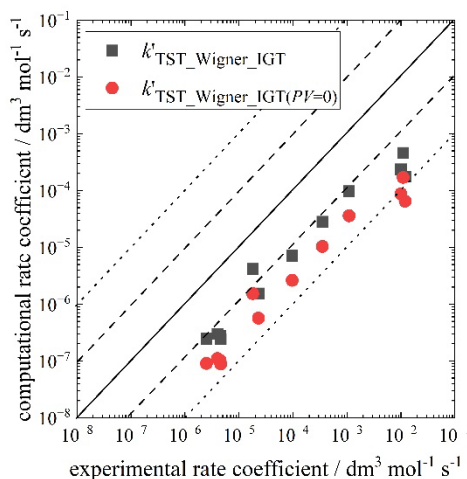
Figure. Correlations between experimental and computational k values for 12 bimolecular Diels-Alder reactions in various solutions and at various temperatures. The predicted k generated by both the new model and the IGT (w_{PV} is ignored) have been corrected using Wigner's tunneling effect.