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Supporting Information

Reaction Mechanisms and Rate Constants of Auto-Catalytic Urethane Formation and Cleavage Reactions

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Experimental Setup and Details on HPLC Measurements

High pressure chromatography method:

For quantitative HPLC analysis an Agilent Technologies series 1200 with UV detector and a chromatographic column of the model Water Symmetry Shield RP 18 was used. Separation of the substances was achieved using the following method. Mobile phase: methanol/water (60/40, vol./vol.) for two minutes changing to methanol/water (70/30, vol./vol.) for another 13 minutes and finishing with methanol/water (90/10, vol./vol.) within another 15 minutes. The samples were diluted in methanol. Flow rate: 0.7 ml/min; column temperature: 40 °C, wavelength of detection: 256 and 260 nm.

Experimental setup:

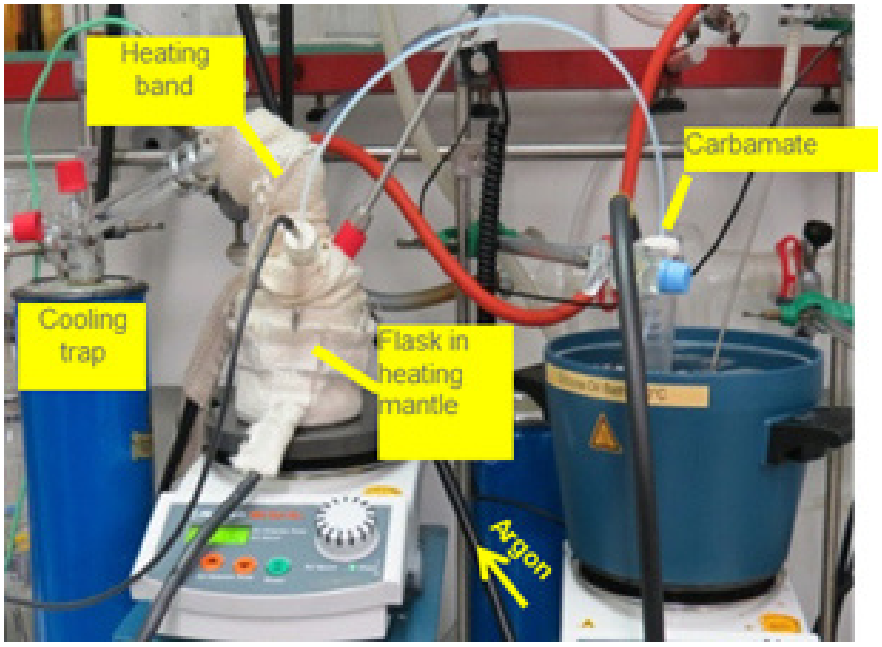

Figure 1: Setup for urethane cleavage experiment.

Experimental Data from the Urethane Cleavage Experiment

$T = 220\,^{\circ}\mathrm{C}$	
t in s	c_{carb} in $\mathrm{mol\,l^{-1}}$
0	1,065655971
300	1,055600366
450	1,046590785
600	1,040945452
1200	0,986461768
1800	0,97559329
3600	0,894210804
5400	0,833302076
7200	0,797802034

Details on Conformer Treatment

Conformer Treatment for Reactants

In case of several relevant reactant conformers $\tilde{i}$, the Gibbs free energy G_i of a reactant i in solution is calculated considering all these conformers. For this purpose, the Gibbs free energy $G_i^{\mathrm{i.G.}}$ in the ideal gas reference state is calculated as follows:

$$G_i^{\mathrm{i.G.}} = \sum_{\tilde{i}} \left[G_{\tilde{i}}^{\mathrm{i.G.}} \frac{\exp\left(-\frac{G_{\tilde{i}}^{\mathrm{i.G.}} - G_0^{\mathrm{i.G.}}}{RT}\right)}{\sum_{\tilde{i}} \exp\left(-\frac{G_{\tilde{i}}^{\mathrm{i.G.}} - G_0^{\mathrm{i.G.}}}{RT}\right)} \right] - RT \sum_{\tilde{i}} \left[\frac{\exp\left(-\frac{G_{\tilde{i}}^{\mathrm{i.G.}} - G_0^{\mathrm{i.G.}}}{RT}\right)}{\sum_{\tilde{i}} \exp\left(-\frac{G_{\tilde{i}}^{\mathrm{i.G.}} - G_0^{\mathrm{i.G.}}}{RT}\right)} \ln\left(\frac{\exp\left(-\frac{G_{\tilde{i}}^{\mathrm{i.G.}} - G_0^{\mathrm{i.G.}}}{RT}\right)}{\sum_{\tilde{i}} \exp\left(-\frac{G_{\tilde{i}}^{\mathrm{i.G.}} - G_0^{\mathrm{i.G.}}}{RT}\right)} \right) \right].$$

Here, $G_{\tilde{i}}^{\mathrm{i.G.}}$ denotes the Gibbs free energy of a conformer $\tilde{i}$ in the ideal gas reference state and $G_0^{\mathrm{i.G.}}$ the Gibbs free energy of the most stable conformer. The sums run over all relevant conformers of reactant i. The second term in the equation accounts for the entropy of ideal mixing.

Accordingly, all relevant conformers are considered in the calculation of the solvation free energy $\Delta G_i^{\mathrm{solv}}$ of reactant i with COSMO-RS.[1–3]

Treatment of Transition State Conformers

As already outlined in the manuscript, the conformers of transition states (TS) are treated by computing individual rate constants $\tilde{k}$ for reaction via the individual TS conformers. Subsequently, the contributions are summed up in the calculation of the rate constant k:

$$k = \sum \tilde{k} \tag{1}$$

The sum runs over all TS conformers. This treatment is discussed more detail elsewhere.[4]

Molecular Geometries and Energies Obtained from Quantum Chemical Calculations

MeOH

$E_{\mathrm{DLPNO-CCSD(T)/aug-cc-pVTZ}} = -115.561994892551$

C	0.66662900	0.02005800	-0.00001100
H	1.03385300	0.54509200	0.89023000
H	1.08470800	-0.98599200	0.00217000
H	1.03427100	0.54161100	-0.89218000
O	-0.75049100	-0.12191400	-0.00003000
H	-1.14867700	0.75425300	0.00009000

PhenylNCO

$E_{\text{DLPNO-CCSD(T)/aug-cc-pVTZ}} = -399.063149242343$

C	0.09126300	-0.25261600	-0.00073700
N	1.44738200	-0.58326000	-0.00155300
C	2.53680600	-0.08079500	0.00003600
O	3.64380100	0.30016900	0.00142500
C	-0.84451100	-1.28764900	-0.00008300
C	-2.20179100	-0.99089200	0.00065300
C	-2.63465800	0.33187800	0.00069200
C	-1.69792400	1.36205900	-0.00002400
C	-0.33857300	1.07802200	-0.00077400
H	-0.49575900	-2.31172100	-0.00013800
H	-2.92338800	-1.79829300	0.00118400
H	-3.69303000	0.55910000	0.00128400
H	-2.02523200	2.39439100	-0.00002900
H	0.39165600	1.87795800	-0.00140400

MPCtrans

$E_{\text{DLPNO-CCSD(T)/aug-cc-pVTZ}} = -514.667401361183$

C	3.48738000	0.31429000	0.00129800
C	2.53177000	1.32434400	0.00045500
C	1.17132000	1.03336500	-0.00076200
C	0.75491800	-0.30147300	-0.00107300
C	1.71540000	-1.32044600	-0.00026600
C	3.06820800	-1.01302700	0.00092800
H	4.54258300	0.55584600	0.00221500
H	2.84246600	2.36211100	0.00072000
H	0.43871200	1.82438300	-0.00146900
H	1.39901300	-2.35813800	-0.00055100
H	3.79556100	-1.81558200	0.00157400
N	-0.59748500	-0.69305700	-0.00248700
H	-0.77999600	-1.68462200	-0.00117900
C	-1.71332100	0.09742400	-0.00081800
O	-1.75486700	1.30620900	-0.00064700
O	-2.81313900	-0.70437300	0.00097700
C	-4.07286900	-0.01386500	0.00160200
H	-4.16870400	0.61207100	0.88919500
H	-4.17024900	0.61080100	-0.88672600
H	-4.82976700	-0.79384000	0.00282400

MPCcis

$E_{\mathrm{DLPNO-CCSD(T)/aug-cc-pVTZ}} = -514.663607655099$

C	-3.28676700	0.64066600	0.06607100
C	-2.19366100	1.46702400	-0.16855300
C	-0.90429400	0.95212100	-0.25204500
C	-0.69390700	-0.41944400	-0.08419500
C	-1.79571000	-1.25169800	0.15191600
C	-3.07769900	-0.72623100	0.22233100
H	-4.28558300	1.05356100	0.12547000
H	-2.33978700	2.53258800	-0.29816800
H	-0.06991500	1.60691200	-0.44128100
H	-1.64307800	-2.31704700	0.28638000
H	-3.91423600	-1.38929000	0.40575000
N	0.56778700	-1.04547400	-0.17630700
H	0.55243100	-2.05107400	-0.25215900
C	1.85547100	-0.58223600	-0.06828400
O	2.81889600	-1.31597500	-0.12930200
O	1.92903300	0.75194000	0.11261600
C	3.26259000	1.27665600	0.24814900
H	3.76093200	0.83717800	1.11191900
H	3.84898200	1.06909600	-0.64666900
H	3.13619000	2.34753300	0.38405600

Urethane Formation, TS with 4-ring

$E_{\mathrm{DLPNO-CCSD(T)/aug-cc-pVTZ}} = -514.5811796$

C	3.48556500	0.05520000	-0.13635500
C	2.67004400	1.18299800	-0.13981000
C	1.28885900	1.06302800	-0.03936800
C	0.70863600	-0.20670700	0.06838800
C	1.52764200	-1.33954700	0.07212100
C	2.90586400	-1.20628000	-0.02945600
H	4.56047000	0.15790400	-0.21498000
H	3.11031900	2.16939500	-0.22204000
H	0.66220400	1.94476400	-0.04349800
H	1.07051300	-2.31747500	0.15752600
H	3.52931100	-2.09212300	-0.02445900
N	-0.67743700	-0.40747200	0.17000500
H	-1.78282500	-1.18629300	0.29409000
C	-1.58920300	0.52415800	0.20534000
O	-1.84752700	1.67816600	0.12733000
O	-2.79082000	-0.58387300	0.43636500
C	-3.83206500	-0.56114500	-0.54891900
H	-4.26048600	0.44150300	-0.56213800
H	-3.43985700	-0.80695100	-1.53984700
H	-4.59287000	-1.28299600	-0.25589500

Urethane Formation, TS with 6-ring, Conformer 1

$E_{\mathrm{DLPNO-CCSD(T)/aug-cc-pVTZ}} = -630.1843287$

C	3.95552900	0.12930200	-0.03807600
C	3.31453100	-1.08734100	0.17111100
C	1.92642600	-1.17631600	0.17878400
C	1.14940500	-0.02667300	-0.02432900
C	1.80235800	1.19623400	-0.23377400
C	3.18756300	1.27299500	-0.24148800
H	5.03679600	0.18653700	-0.04309600
H	3.89949500	-1.98561400	0.32992500
H	1.44555300	-2.12981300	0.33854400
H	1.20702700	2.08753300	-0.39431200
H	3.66875600	2.22955400	-0.40715800
N	-0.25805200	0.00786300	-0.02896400
H	-1.11537300	1.23145900	-0.34940000
C	-0.97906200	-1.06474000	0.10741000
O	-0.87426400	-2.25383300	0.21797300
O	-2.49320400	-0.55610600	0.14547300
C	-3.48261200	-1.45945600	-0.37517300
H	-3.48776400	-1.43373800	-1.46664000
H	-3.23929700	-2.46084200	-0.02860200
H	-4.44903600	-1.14968200	0.01889900
C	-2.25268700	2.68682000	0.56827900
H	-1.64767600	3.56708800	0.34694700
H	-1.97077600	2.29128400	1.54854900
H	-3.30349100	2.97394200	0.58156600
O	-2.06363600	1.70506900	-0.46049100
H	-2.51772800	0.55125100	-0.17257400

Urethane Formation, TS with 6-ring, Conformer 2

$E_{\mathrm{DLPNO-CCSD(T)/aug-cc-pVTZ}} = -630.1836063$

C	3.95084500	0.10907600	0.12158900
C	3.28467100	-1.09718200	0.31150000
C	1.90119200	-1.18043600	0.19337100
C	1.15490800	-0.03584900	-0.12259900
C	1.83330000	1.17594500	-0.31571800
C	3.21352500	1.24737500	-0.19456500
H	5.02824800	0.16198200	0.21568300
H	3.84595100	-1.99137300	0.55585500
H	1.40021000	-2.12500800	0.34429300
H	1.26214100	2.06054100	-0.57238500
H	3.71515500	2.19503600	-0.35049400
N	-0.24527200	0.00428000	-0.26167800
H	-1.08603000	1.27444700	-0.42675200
C	-0.98781800	-1.05365400	-0.12911100
O	-0.91496600	-2.22182900	0.13242200
O	-2.47292800	-0.56374900	-0.44223100
C	-3.54596300	-1.32026000	0.13831200
H	-3.28954600	-2.37459600	0.07044400
H	-3.69202600	-1.04371800	1.18486000
H	-4.44377000	-1.11270300	-0.44135400
C	-2.20889700	2.52921300	0.75631500
H	-1.59567100	3.43039500	0.71793300
H	-1.92999600	1.94445400	1.63864100
H	-3.25718900	2.81753200	0.82763600
O	-2.02658200	1.77327300	-0.44802300
H	-2.49935200	0.58613600	-0.42453100

Urethane Formation, TS with 8-ring, Conformer 1

$E_{\mathrm{DLPNO-CCSD(T)/aug-cc-pVTZ}} = -745.770201$

C	4.22467600	0.20026000	0.29701000
C	3.69829500	-1.05828000	0.02586400
C	2.32896600	-1.24762400	-0.13045800
C	1.44824100	-0.16002400	-0.01561600
C	1.98896300	1.10717300	0.25845400
C	3.35687400	1.28319800	0.41178200
H	5.29238800	0.33594600	0.41672200
H	4.36005300	-1.91165100	-0.06724500
H	1.94057500	-2.23273600	-0.33904400
H	1.31934900	1.95368300	0.35089700
H	3.74615300	2.27223500	0.62354200
N	0.04594900	-0.22313800	-0.15987100
H	-2.28279700	1.56482100	0.30979100
C	-0.56472700	-1.36479100	-0.27655700
O	-0.32034600	-2.54411500	-0.33236000
O	-2.08937200	-1.04634900	-0.35875400
C	-2.96562300	-2.18742200	-0.39022800
H	-2.85885900	-2.78261000	0.51659700
H	-3.97851900	-1.79771900	-0.48006500
H	-2.71732500	-2.80091200	-1.25219800
C	-2.29306200	0.91566800	2.23293100
H	-2.52698700	1.88112600	2.67929400
H	-1.21422700	0.74983600	2.23372100
H	-2.79196800	0.12728000	2.79348700
O	-2.80533600	0.88553600	0.88134700
H	-2.46488700	-0.13762600	0.29299800
C	-1.30541100	2.50603400	-1.90153200
H	-0.32823900	2.70134000	-2.35088700
H	-1.81742400	1.73664000	-2.48932200
H	-1.89332400	3.42342500	-1.92958700
O	-1.15705100	2.11401400	-0.53798100
H	-0.63190600	1.24104400	-0.47751800

Urethane Formation, TS with 8-ring, Conformer 2

$E_{\text{DLPNO-CCSD(T)/aug-cc-pVTZ}} = -745.7684745$

C	4.14738200	0.01885900	0.34218900
C	3.60310600	-1.19402800	-0.06893700
C	2.23130600	-1.34780200	-0.23821100
C	1.36340800	-0.27042200	0.00388900
C	1.92390900	0.94760100	0.42123400
C	3.29419100	1.09128500	0.58785500
H	5.21716800	0.12651900	0.47095300
H	4.25410800	-2.03870600	-0.26279400
H	1.82738300	-2.29863900	-0.55122000
H	1.26283600	1.78124700	0.62469100
H	3.69651400	2.04343700	0.91385500
N	-0.03417000	-0.29286200	-0.16120600
H	-2.30018800	1.61714600	0.00235400
C	-0.67842700	-1.42523100	-0.22754900
O	-0.44743000	-2.61068800	-0.21289100
O	-2.16852400	-1.08120400	-0.33634800
C	-3.08062800	-2.19277700	-0.33383200
H	-3.00817800	-2.74955700	0.60034200
H	-4.07758900	-1.77293200	-0.45814400
H	-2.84125300	-2.85268300	-1.16379500
C	-2.29602600	1.16287700	1.98185700
H	-2.50574300	2.17235800	2.33257600
H	-1.22247100	0.96806500	1.98368600
H	-2.80656600	0.44525400	2.62086100
O	-2.82709400	1.01289600	0.64430400
H	-2.53284800	-0.05965900	0.18998100
C	-0.47588600	3.08694100	-1.38677000
H	0.07310200	3.50589800	-0.53662000
H	0.23838400	2.83968700	-2.17580900
H	-1.16753600	3.84051600	-1.76381400
O	-1.23254200	1.93931400	-1.01999600
H	-0.65723500	1.13572100	-0.78958200

Urethane Formation, TS with 8-ring, Conformer 3

$E_{\mathrm{DLPNO-CCSD(T)/aug-cc-pVTZ}} = -745.7684534$

C	-4.12303100	-0.19191300	0.35427600
C	-3.32504900	-1.14677900	0.97849700
C	-1.96010400	-1.21354200	0.72526100
C	-1.35987700	-0.31272100	-0.16701200
C	-2.17270100	0.63983200	-0.79663100
C	-3.53638700	0.69920100	-0.53953300
H	-5.18621100	-0.14843300	0.55519100
H	-3.76909800	-1.85242500	1.67101400
H	-1.35719800	-1.97168300	1.20431500
H	-1.72313100	1.32091300	-1.50862300
H	-4.14327300	1.44147600	-1.04470100
N	0.02550700	-0.25975500	-0.43022800
H	2.20280100	1.69681000	0.02985900
C	0.72721600	-1.35509600	-0.38239900
O	0.56269500	-2.53847200	-0.21319500
O	2.20277400	-0.95734800	-0.62913500
C	3.14720300	-2.04398700	-0.63873100
H	2.89101300	-2.72801200	-1.44358500
H	4.12519200	-1.59939800	-0.81609800
H	3.12931300	-2.58210600	0.30863400
C	2.46031700	0.98409600	1.91522400
H	1.40229900	0.72879500	2.00771200
H	2.65805200	1.94584100	2.38728800
H	3.06718200	0.21830200	2.39483700
O	2.84558900	1.05075400	0.52610000
H	2.55909800	0.01056200	-0.04563400
C	0.18479700	3.21337300	-0.26422100
H	-0.56977500	3.47799000	-1.00872000
H	-0.32540500	2.90527300	0.65369700
H	0.79343600	4.09453300	-0.05924900
O	1.04397600	2.18762600	-0.76155000
H	0.57259000	1.28457400	-0.76048400

TS of Urethane Cleavage

$E_{\mathrm{DLPNO-CCSD(T)/aug-cc-pVTZ}} = -1029.298282$

C	3.96228300	-2.27843500	-0.82919000
C	4.38936000	-1.20477200	-0.05347400
C	3.54436400	-0.13434400	0.21797900
C	2.23602900	-0.11910600	-0.29086000
C	1.81710300	-1.20367400	-1.07674500
C	2.66747400	-2.26823000	-1.34065900
H	4.62826900	-3.10721000	-1.03520200
H	5.39573300	-1.19611900	0.34909100
H	3.89490500	0.69530900	0.81359700
H	0.81330000	-1.20058900	-1.48241800
H	2.31603300	-3.09246800	-1.95018600
N	1.28324300	0.88405900	-0.03111700
H	-0.25764000	0.42260000	0.00290600
C	1.65237100	2.08192800	0.33226900
O	2.67371300	2.69495600	0.53209700
O	0.37907500	2.88805400	0.54865400
C	0.55196700	4.30000000	0.76211500
H	1.21082300	4.45470700	1.61244400
H	0.98298500	4.77201100	-0.12080100
H	-0.43871200	4.70246200	0.96758900
C	-2.00891800	-3.89490900	0.92798900
C	-2.88660400	-3.24630200	0.06618700
C	-2.69704000	-1.91005400	-0.27084100
C	-1.62128600	-1.20849400	0.27573800
C	-0.73343800	-1.85988300	1.13672600
C	-0.92817100	-3.19554300	1.45729700
H	-2.16164900	-4.93673700	1.17995400
H	-3.72445700	-3.78418300	-0.36028300
H	-3.37600000	-1.42197800	-0.95208000
H	0.11393100	-1.31762700	1.53546500
H	-0.22895000	-3.69000300	2.11970700
N	-1.31049000	0.14172800	-0.03418300
H	-0.63060100	2.57253800	-0.04504000
C	-2.11014700	1.13294100	-0.37077800
O	-1.69251900	2.32533700	-0.52398800
O	-3.39812500	0.87619000	-0.55719900
C	-4.26565900	1.99473300	-0.84752600
H	-4.24167100	2.71646100	-0.03227000
H	-3.96457000	2.47863300	-1.77522500
H	-5.25628400	1.56025500	-0.94404600

Experimental Literature Data and Calculated Rate Constants for Urethane Formation

$\log\left(k^{\mathrm{pred}}/\mathrm{m^3\,mol^{-1}\,s^{-1}}\right)$	$\log\left(k^{\mathrm{exp}}/\mathrm{m^3\,mol^{-1}\,s^{-1}}\right)$	T in °C	Solvent	Ref. exp. data
-6,271330907	-6,926892902	20	benzene	[5]
-6,045348257	-6,93305321	20	toluene	[5]
-6,998150653	-7,346787486	20	nitrobenzene	[5]
-7,477582593	-7,547702329	20	di-n-butyl ether	[5]
-7,808791391	-7,736758565	20	n-butyl acetate	[5]
-8,961835761	-8,286789557	20	butanone	[5]
-9,350468534	-8,547702329	20	dioxane	[5]
-9,029070389	-8,77815125	20	acetonitrile	[5]
-5,196439002	-6,187086643	25	cyclohexane	[6]
-5,0032155	-6,187086643	25	n-heptane	[6]
-5,508431932	-6,522878745	25	carbon tetrachloride	[6]
-5,891189245	-6,736758565	25	xylene	[6]
-6,094184588	-6,814363423	25	toluene	[6]
-6,287563836	-6,875061263	25	chlorobenzene	[6]
-6,318570936	-7,014723257	25	benzene	[6]
-7,784893761	-7,315753252	25	chloroform	[6]
-6,978440577	-7,346787486	25	1,2-dichloroethane	[6]
-7,564475883	-7,455931956	25	di-n-butyl ether	[6]
-7,162829843	-7,522878745	25	nitrobenzene	[6]
-9,074679853	-8,259637311	25	methyl ethyl ketone	[6]
-8,09733086	-8,363177902	25	n-butyl acetate	[6]
-8,61372721	-8,522878745	25	ethyl acetate	[6]
-9,886316528	-8,547702329	25	tetrahydrofuran	[6]
-9,167321277	-8,602059991	25	acetonitrile	[6]
-9,475661085	-8,875061263	25	dioxane	[6]
-6,207577644	-6,3400838	25	excess alcohol	[7]
-5,770930317	-6,358525889	25	xylene	[8]

The predicted rate constants k^{pred} were evaluated at the reaction mixture compositions used in the experiments.

Arrhenius Plots

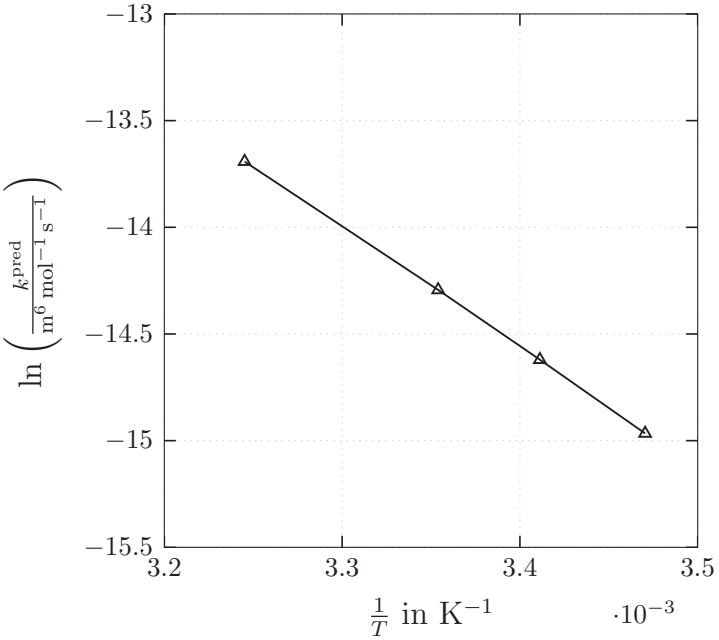

Figure 2: Arrhenius plot for the urethane formation in excess alcohol. The triangles show the predicted reaction rate constants. The solid line shows the fit of the Arrhenius equation.

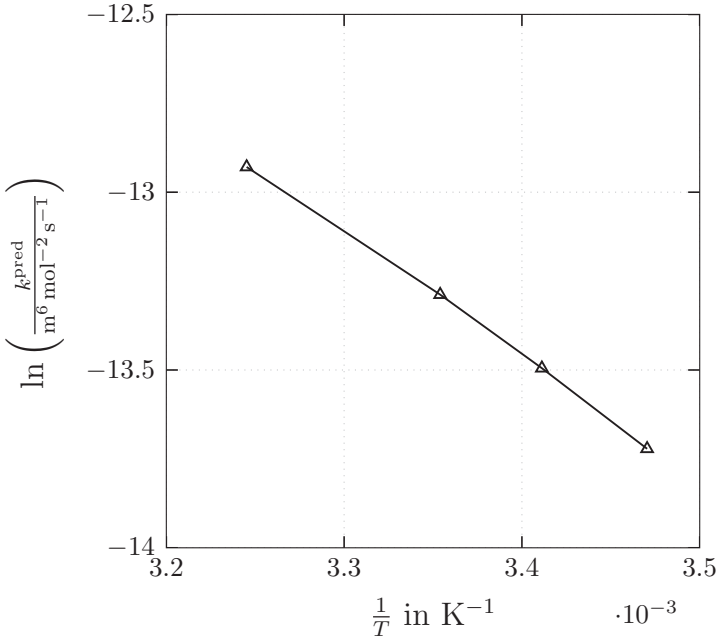

Figure 3: Arrhenius plot for the urethane formation in xylene. The triangles show the predicted reaction rate constants. The solid line shows the fit of the Arrhenius equation.

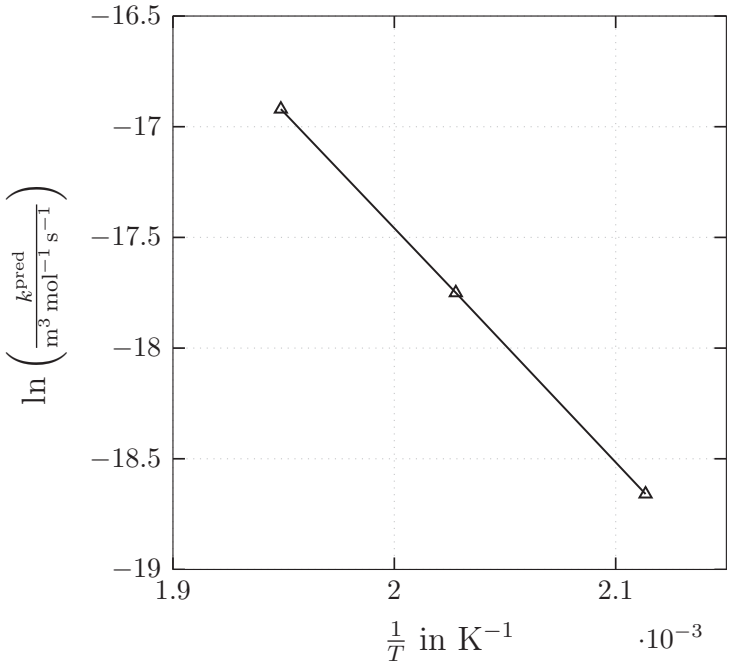

Figure 4: Arrhenius plot for the MPC cleavage reaction in diphenyl ether. The triangles show the predicted reaction rate constants. The solid line shows the fit of the Arrhenius equation.

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