Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Elucidating the reactivity of methoxyphenol positional isomers towards hydrogen-transfer reactions by ATR-IR spectroscopy of the liquid-solid interface of RANEY® Ni

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Supporting information

1 – H-transfer at different initial substrate concentration

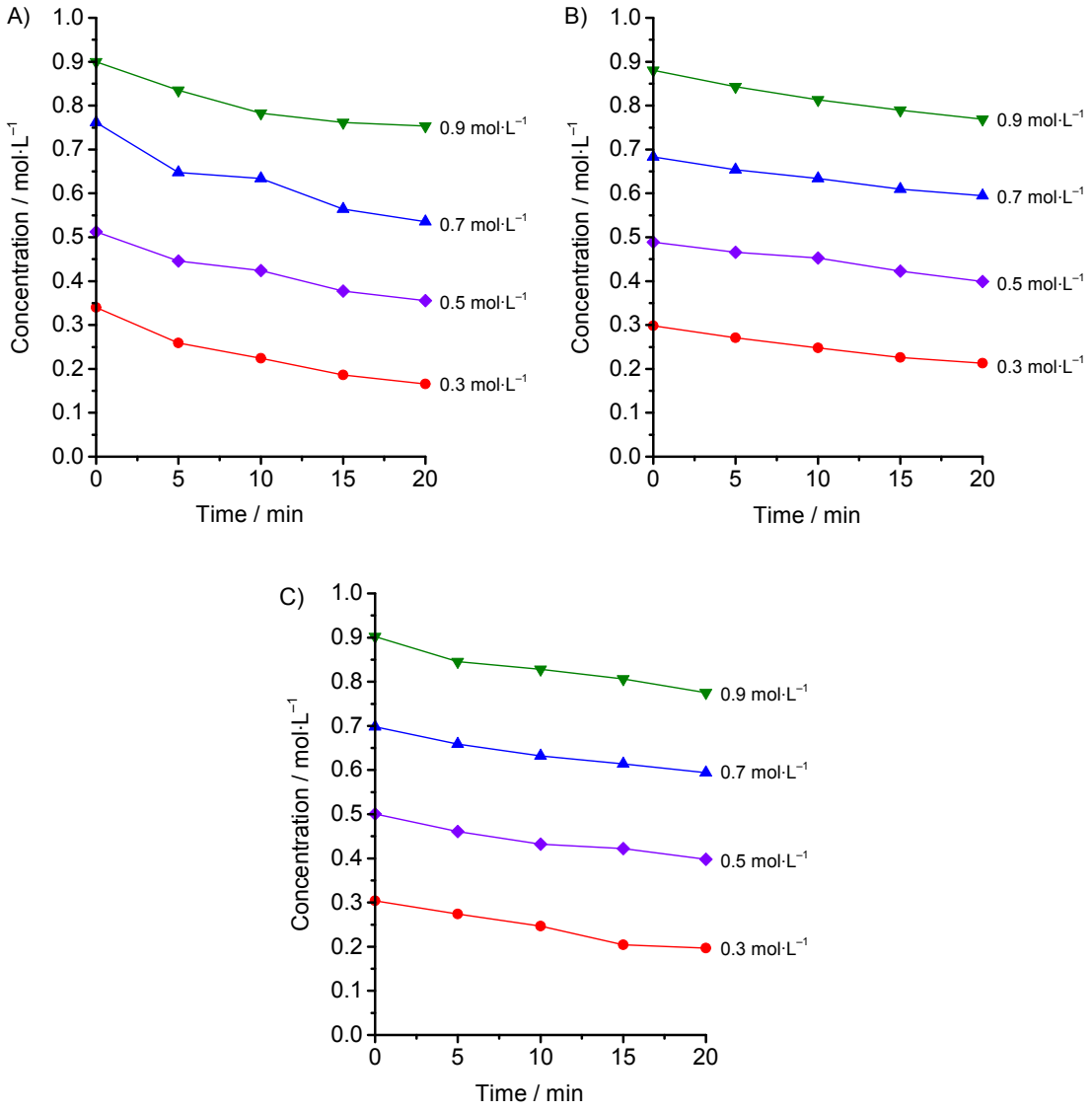

Figure S1. Evolution of the reactant concentration at 80 °C as a function of time using different initial substrate concentrations for A) 2-methoxyphenol, B) 3-methoxyphenol and C) 4-methoxyphenol in the presence of RANEY® Ni/2-PrOH.

2 – Arrhenius equation

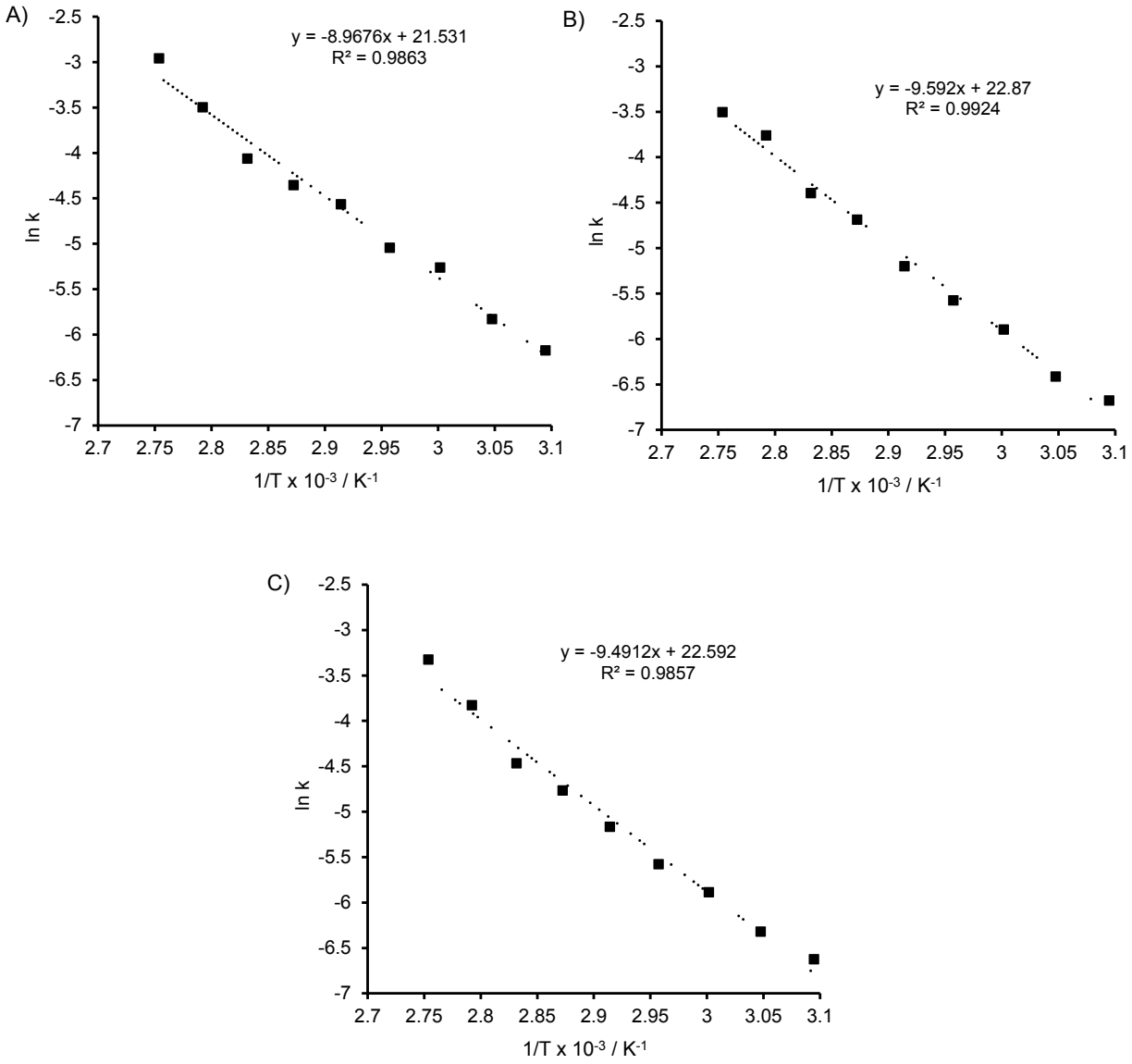

Figure S2. Arrhenius plots for A) 2-methoxyphenol, B) 3-methoxyphenol and C) 4-methoxyphenol in the presence of RANEY® Ni/2-PrOH.

3 - ATR-IR spectroscopy bands assignment by DFT calculation

Table S1. ATR-IR spectroscopy bands assignment by DFT calculation for phenol.

Phenol			
exp	B3LYP [def2-SV(P)]		assignment[c]
ν	ω^a	A[b]	
3617	3447	50	ν(OH)
1607	1607	54	$\nu(C\text{-}C)_{arom}$
1597	1590	32	$\nu(C\text{-}C)_{arom}$
1499	1490	51	$\nu(C\text{-}C)_{arom}$, δ(C-H)
1474	1464	38	$\nu(C\text{-}C)_{arom}$, δ(C-H)
1340	1345	58	δ(O-H), $\delta(C\text{-}H)_{arom}$
1256	1266	87	ν(C-O), $\delta(C\text{-}H)_{arom}$
1174	1189	126	$\nu(C\text{-}C)_{arom}$, δ(O-H), $\delta(C\text{-}H)_{arom}$

[a] The scaling factor for frequencies was 0.972.

[b] Signals below an intensity of 20 were not considered.

[c] Assignment in agreement with reference [42].

Table S2. ATR-IR spectroscopy bands assignment by DFT calculation for 2-methoxyphenol.

2-methoxyphenol			
exp	B3LYP [def2-SV(P)]		assignment
ν	ω^a	A[b]	
3562	3374	43	ν(OH)
overlap with solvent	2975	20	$\nu(C\text{-}H)_{aliphat}$
	2901	37	$\nu(C\text{-}H)_{aliphat}$
	2838	55	$\nu(C\text{-}H)_{aliphat}$
1600	1594	38	$\nu(C\text{-}C)_{arom}$, δ(O-H), $\nu(C\text{-}O)_{arom}$
1502	1502	182	$\nu(C\text{-}O)_{arom}$, $\nu(C\text{-}C)_{arom}$, $\delta(C\text{-}H)_{aliphat}$, $\delta(C\text{-}H)_{arom}$
1472	1466	27	$\nu(C\text{-}C)_{arom}$, $\delta(C\text{-}H)_{aliphat}$, $\delta(C\text{-}H)_{arom}$, δ(O-H)
1456	1460	38	$\delta(C\text{-}H)_{aliphat}$, $\delta(C\text{-}H)_{arom}$
	1382	77	δ(O-H), $\nu(C\text{-}C)_{arom}$, $\delta(C\text{-}H)_{arom}$
	1304	22	δ(O-H), $\nu(C\text{-}C)_{arom}$, $\delta(C\text{-}H)_{arom}$
1260	1271	197	$\nu(C\text{-}OH)_{arom}$, $\delta(C\text{-}H)_{arom}$, $\nu(C\text{-}C)_{arom}$
1223	1238	169	$\nu(C\text{-}OMe)_{arom}$, $\nu(C\text{-}C)_{arom}$, $\delta(C\text{-}H)_{arom}$
1205	1211	54	δ(O-H), $\delta(C\text{-}H)_{aliphat}$, $\delta(C\text{-}H)_{arom}$
1175	1181	24	δ(O-H), $\delta(C\text{-}H)_{aliphat}$, $\delta(C\text{-}H)_{arom}$
1111	1103	38	$\delta(C\text{-}H)_{arom}$
1043	1044	43	$\nu(C\text{-}O)_{aliphat}$, $\delta(C\text{-}H)_{arom}$
1027	1019	21	$\delta(C\text{-}H)_{arom}$

[a] The scaling factor for frequencies was 0.973.

[b] Signals below an intensity of 20 were not considered.

Table S3. ATR-IR spectroscopy bands assignment by DFT calculation for 3-methoxyphenol.

3-methoxyphenol			
exp	B3LYP [def2-SV(P)]		assignment
ν	ω^a	A[b]	
3618	3456	53	ν(OH)
overlap with solvent	2971	24	$\nu(C\text{-}H)_{aliphat}$
	2895	40	$\nu(C\text{-}H)_{aliphat}$
	2833	53	$\nu(C\text{-}H)_{aliphat}$
1615	1615	150	$\nu(C\text{-}C)arom$, $\nu(C\text{-}O)_{arom}$
1596	1589	136	$\nu(C\text{-}C)arom$, $\nu(C\text{-}O)_{arom}$
1493	1492	97	$\nu(C\text{-}C)arom$, $\nu(C\text{-}O)_{arom}$
1470	1459	57	$\delta(C\text{-}H)_{aliphat}$
1437	1442	33	$\delta(C\text{-}H)_{aliphat}$, $\delta(C\text{-}H)_{arom}$
1328	1338	87	$\nu(C\text{-}C)_{arom}$, $\nu(C\text{-}O)_{arom}$
1302	1309	46	$\delta(C\text{-}H)_{arom}$, $\delta(O\text{-}H)_{arom}$
1288	1294	102	$\nu(C\text{-}O)_{arom}$, δ(O-H), $\delta(C\text{-}H)_{arom}$
	1219	78	$\nu(C\text{-}O)_{arom}$, δ(O-H), $\delta(C\text{-}H)_{arom}$
1198	1198	87	δ(O-H), $\delta(C\text{-}H)_{aliphat}$
1170	1171	125	$\nu(C\text{-}O)_{arom}$, $\delta(C\text{-}H)_{arom}$, $\delta(C\text{-}O)_{aliphat}$
1150	1141	29	$\delta(C\text{-}H)_{arom}$
1045	1048	38	$\nu(C\text{-}O)_{aliphat}$, $\delta(C\text{-}H)_{arom}$

[a] The scaling factor for frequencies was 0.973.

[b] Signals below an intensity of 20 were not considered.

Table S4. ATR-IR spectroscopy bands assignment by DFT calculation for 4-methoxyphenol.

4-methoxyphenol			
exp	B3LYP [def2-SV(P)]		assignment
v	*ω*[a]	A[b]	
3622	3459	54	ν(OH)
overlap with solvent	2968	25	$\nu(C\text{-}H)_{aliphat}$
	2882	47	$\nu(C\text{-}H)_{aliphat}$
	2825	63	$\nu(C\text{-}H)_{aliphat}$
1511	1511	229	$\nu(C\text{-}C)_{arom}$, $\nu(C\text{-}O)_{arom}$, $\delta(C\text{-}H)_{arom}$, $\delta(C\text{-}H)_{aliphat}$
1488	1460	70	$\delta(C\text{-}H)_{aliphat}$
1465	1435	51	$\nu(C\text{-}C)_{arom}$, δ(O-H), $\delta(C\text{-}H)_{arom}$, $\delta(C\text{-}H)_{aliphat}$
1354	1345	88	$\nu(C\text{-}C)_{arom}$, δ(O-H), $\delta(C\text{-}H)_{arom}$
1297	1294	21	$\nu(C\text{-}C)_{arom}$, $\delta(C\text{-}H)_{arom}$
1236	1249	291	$\nu(C\text{-}O)_{arom}$, $\delta(C\text{-}H)_{arom}$
1173	1195	107	δ(O-H), $\delta(C\text{-}H)_{arom}$, $\delta(C\text{-}H)_{aliphat}$
1163	1183	78	$\nu(C\text{-}C)_{arom}$, δ(O-H), $\delta(C\text{-}H)_{arom}$, $\delta(C\text{-}H)_{aliphat}$
1046	1053	66	$\nu(C\text{-}O)_{aliphat}$

[a] The scaling factor for frequencies was 0.973.

[b] Signals below an intensity of 20 were not considered.

4 – Eyring–Polanyi equation

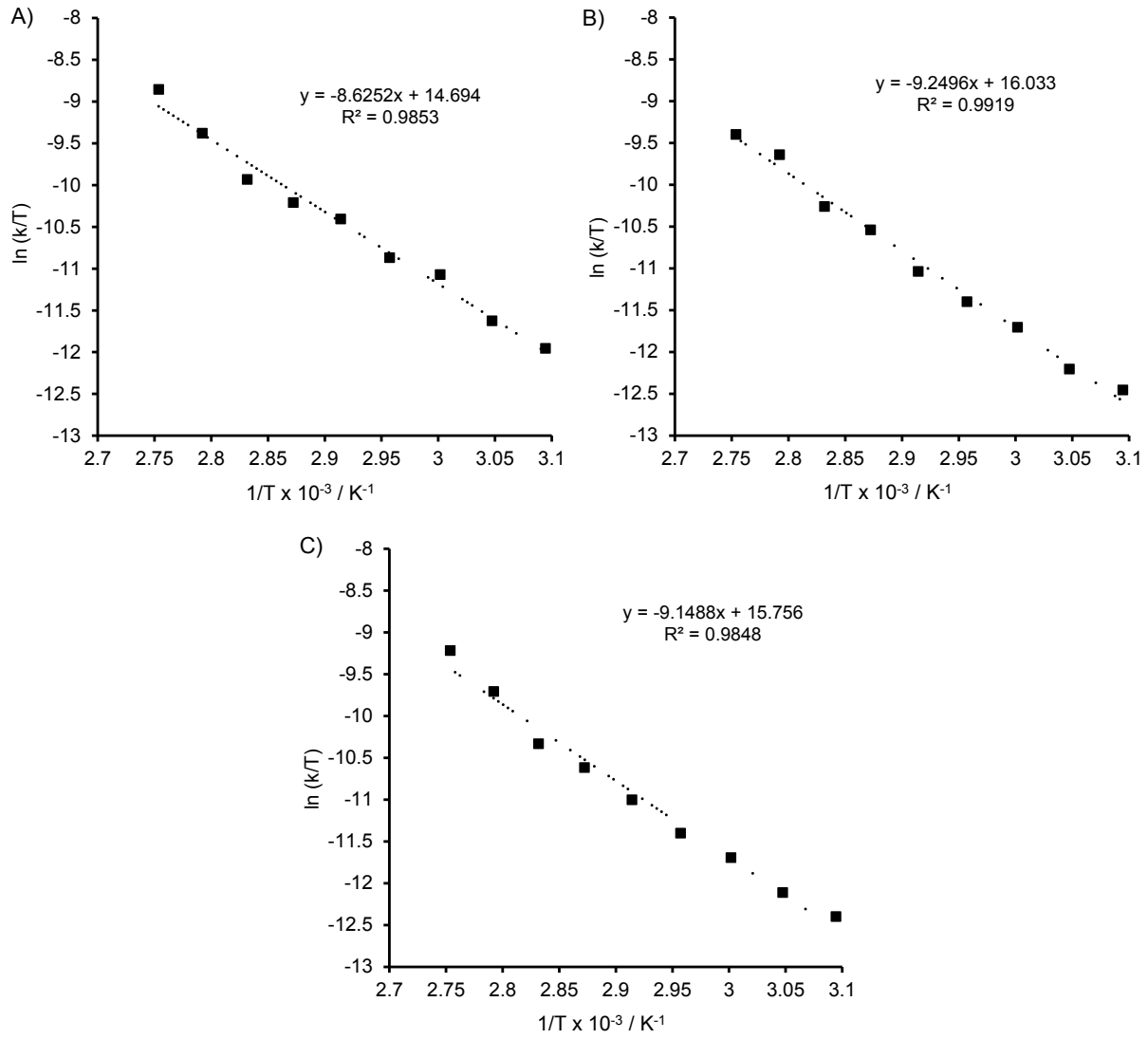

Figure S3. Eyring–Polanyi plots for A) 2-methoxyphenol, B) 3-methoxyphenol and C) 4-methoxyphenol in the presence of RANEY® Ni/2-PrOH.