

Supporting Information

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Hydrothermal Reaction Kinetics and Pathways of Phenylalanine Alone and in Binary Mixtures

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Table 1: Conversion and yields of phenylalanine and phenylethylamine in presence of different additives at 250 °C and 30 min batch holding times

Salt	C _{salt} (mol/L)	Ionic Strength (mol/L)	Phenylalanine Conversion	Phenylethylamine Yield	Carbon Balance (%)
None	-	-	0.33 ± 0.03	0.20 ± 0.04	88 ± 8
NaCl	0.069	0.069	0.46 ± 0.02	0.14 ± 0.01	66 ± 1
NaNO ₃	0.047	0.047	0.55 ± 0.03	0.17 ± 0.01	60 ± 2
Na ₂ SO ₄	0.028	0.085	0.46 ± 0.03	0.13 ± 0.02	65 ± 1
KCl	0.054	0.054	0.38 ± 0.06	0.11 ± 0.01	70 ± 4
K ₂ HPO ₄	0.023	0.069	0.57 ± 0.04	0.11 ± 0.01	53 ± 4
H ₃ BO ₃	0.065	0.387	0.46 ± 0.02	0.10 ± 0.01	62 ± 2

Table 2: Conversion and yields of products for phenylalanine in HTW at different initial concentrations

Temp (°C)	Initial Loading (ppm)	Time (min)	Phenylalanine Conversion	Phenylethylamine Yield	Styrene Yield	Carbon Balance (%)
250	4000	30	0.38	0.22	0	84
		60	0.53	0.27	0	73
		90	0.60	0.33	0	74
		120	0.64	0.42	0.01	79
		150	0.77	0.37	0.02	62
	22000	30	0.34	0.24	0	90
		60	0.48	0.35	0	88
		90	0.59	0.39	0.01	81
		120	0.66	0.40	0.01	75
		150	0.70	0.39	0.02	73
350	4000	10	0.98	0.58	0.04	63
		20	0.98	0.44	0.22	68
		30	0.99	0.43	0.23	68
		40	0.98	0.39	0.27	69
		60	1.00	0.13	0.35	48
	22000	10	1.00	0.71	0.08	78
		20	1.00	0.40	0.21	60
		30	1.00	0.32	0.26	57
		40	1.00	0.24	0.27	50
		60	1.00	0.12	0.43	53

Table 3: Effect of ethyl oleate on yields of products (based on phenylalanine) for binary mixture at 350 °C and different batch holding times

Molar Ratio EO:Phe	Time (min)	Phenylethylamine Yield	Styrene Yield	Phenylethanol Yield	Phenylacet-aldehyde Yield	Overall Carbon Balance (%)
0.2	10	0.51 ± 0.02	0.14 ± 0.02	0.012 ± 0.003	0.0006 ± 0.0003	74 ± 5
	20	0.35 ± 0.01	0.30 ± 0.03	0.030 ± 0.005	0.0013 ± 0.0009	75 ± 1
	30	0.28 ± 0.05	0.35 ± 0.06	0.037 ± 0.009	0.0013 ± 0.0005	71 ± 1
	40	0.18	0.43	0.047	0.0015	68
	60	0.07	0.47	0.055	0.0024	60
1.0	10	0.36 ± 0.02	0.19 ± 0.04	0.026 ± 0.002	0.0014 ± 0.0004	81 ± 3
	20	0.24 ± 0.02	0.31 ± 0.02	0.039 ± 0.001	0.0017 ± 0.0007	78 ± 2
	30	0.16 ± 0.02	0.34 ± 0.03	0.044 ± 0.001	0.0016 ± 0.001	73 ± 7
	40	0.16	0.41	0.054	0.0017	52
	60	0.07	0.39	0.060	0.0031	74
5.0	10	0.30 ± 0.04	0.18 ± 0.03	0.027 ± 0.002	0.014 ± 0.0006	82 ± 5
	20	0.16 ± 0.01	0.33 ± 0.02	0.044 ± 0.004	0.013 ± 0.013	79 ± 1
	30	0.13 ± 0.01	0.37 ± 0.01	0.051 ± 0.003	0.016 ± 0.014	77 ± 5
	40	0.08	0.38	0.054	0.024	81
	60	0.05	0.41	0.068	0.037	77

Table 4: Effect of phenylalanine on yields of products and conversion of ethyl oleate (based on limiting reactant) for binary mixture at 350 °C and different batch holding times

Molar Ratio Phe:EO	Time (min)	ODM Yield	EODM Yield	PEODM Yield	Oleic Acid Yield	Ethyl Oleate Conversion
0.2	10	0.021 ± 0.002	0.007 ± 0.002	0.164 ± 0.054	0.67 ± 0.03	0.81 ± 0.05
	20	0.022 ± 0.003	0.023 ± 0.002	0.161 ± 0.012	0.83 ± 0.01	0.99 ± 0.003
	30	0.024 ± 0.002	0.026 ± 0.002	0.142 ± 0.024	0.82 ± 0.05	0.99 ± 0.005
	40	0.030	0.032	0.122	0.89	1.00
	60	0.032	0.032	0.071	0.84	1.00
1.0	10	0.008 ± 0.002	0.007 ± 0.003	0.149 ± 0.011	0.76 ± 0.02	0.96 ± 0.02
	20	0.013 ± 0.001	0.015 ± 0.003	0.156 ± 0.010	0.73 ± 0.01	0.99 ± 0.003
	30	0.019 ± 0.002	0.014 ± 0.003	0.117 ± 0.017	0.72 ± 0.06	0.99 ± 0.003
	40	0.026	0.021	0.139	0.86	0.99
	60	0.031	0.014	0.055	0.82	1.00
5.0	10	0.011 ± 0.003	0.026 ± 0.002	0.142 ± 0.033	0.78 ± 0.13	0.96 ± 0.003
	20	0.020 ± 0.002	0.024 ± 0.007	0.235 ± 0.018	0.67 ± 0.02	0.99 ± 0.004
	30	0.020 ± 0.006	0.021 ± 0.004	0.224 ± 0.031	0.62 ± 0.04	0.99 ± 0.006
	40	0.031	0.019	0.152	0.62	0.98
	60	0.032	0.024	0.087	0.63	1.00

Table 5: Molar yield of oleic acid and conversion of ethyl oleate at 350 °C and different batch holding times

Time (min)	Oleic Acid Yield	Ethyl Oleate Conversion	Carbon Balance (%)
10	0.31 ± 0.04	0.45 ± 0.02	81 ± 3
20	0.78 ± 0.07	0.98 ± 0.01	85 ± 8
30	0.79 ± 0.04	0.99 ± 0.01	83 ± 4
40	0.81	1.00	80
60	0.73	1.00	73

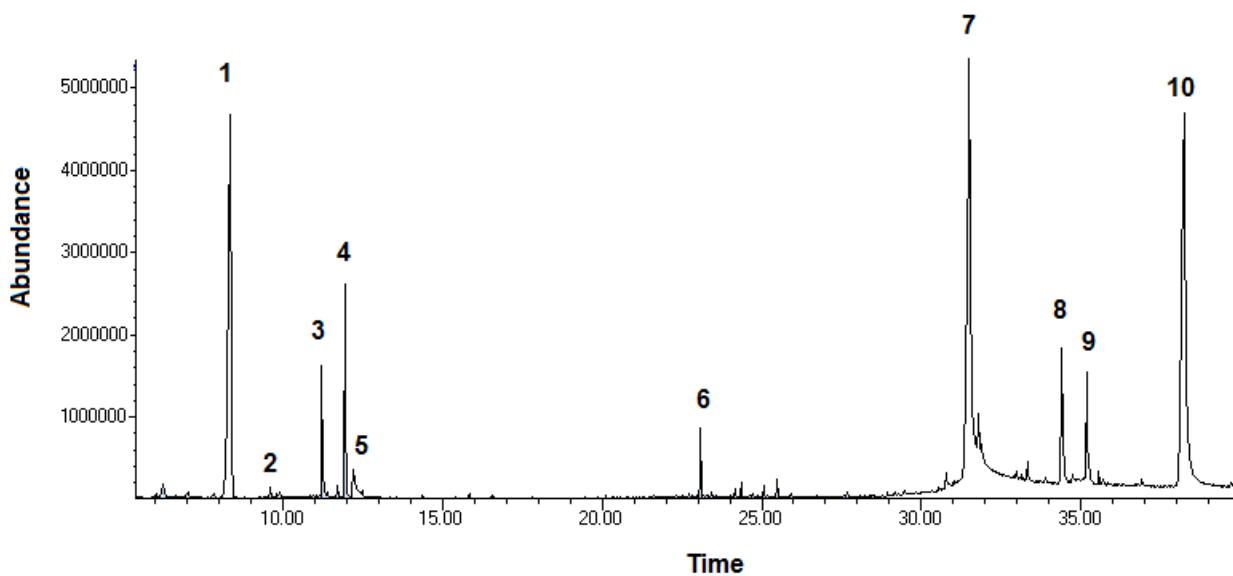
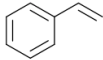
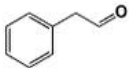
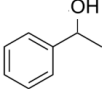
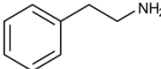
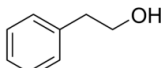
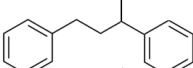
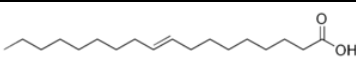
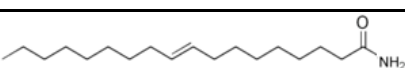
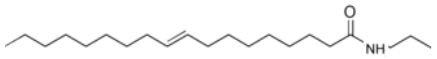
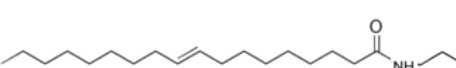


Figure 1: GC-MS chromatogram for binary mixture of phenylalanine and ethyl oleate (1.0 : 1.0) at 350 °C and 30 minutes

Table 6: Chemical names and structure of labels for GC-MS chromatogram for binary mixture of phenylalanine and ethyl oleate (1 : 1) at 350 °C and 30 min

Peak No.	Chemical Name	Structure
1	Styrene	
2	Phenylacetaldehyde	
3	1-phenylethanol	
4	Phenylethylamine	
5	2-phenylethanol	
6	1,3-diphenylbutane	
7	Oleic Acid	
8	9-octadecenamide	
9	N-ethyl-9-octadecenamide	
10	N-phenylethyl-9-octadecenamide	

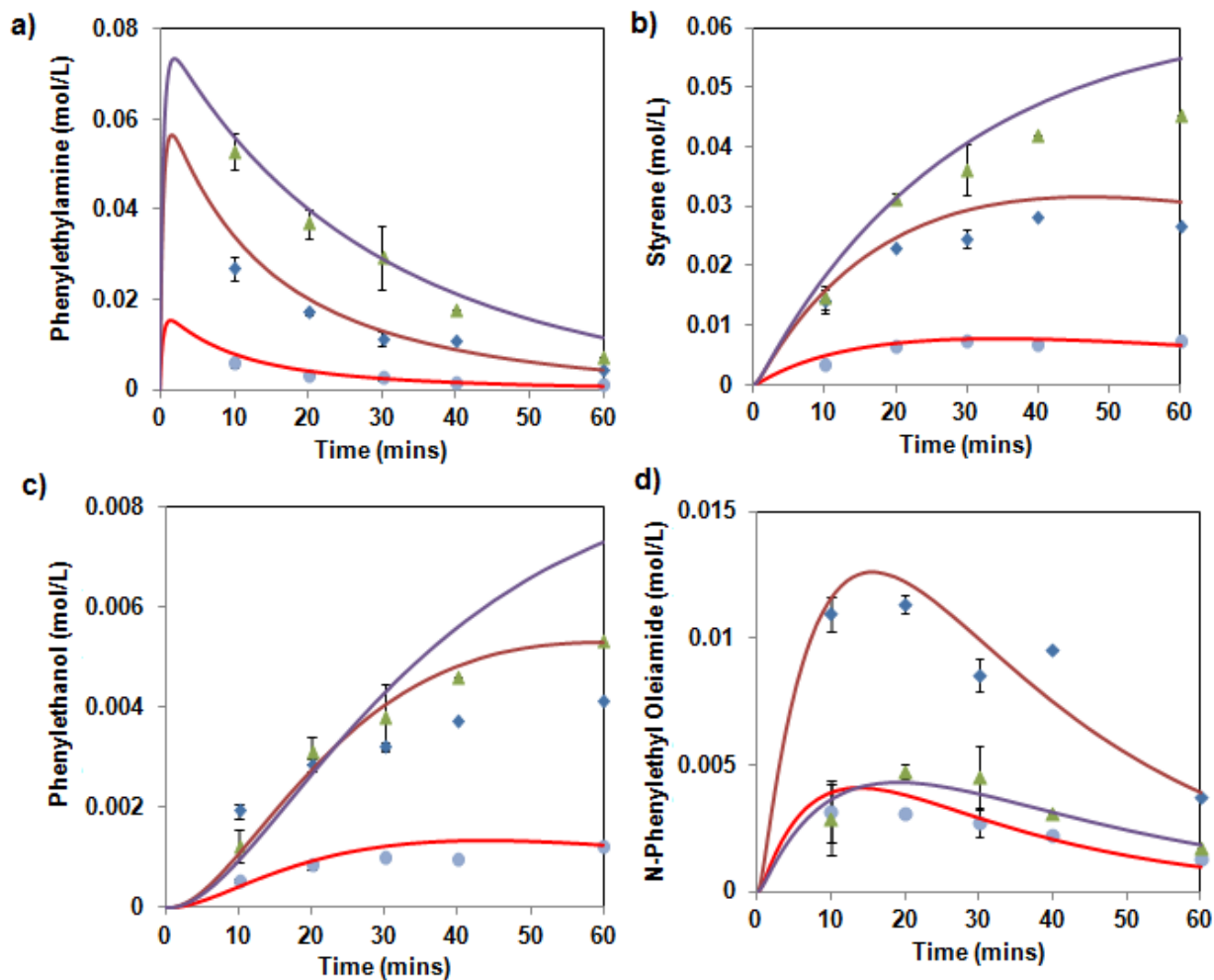


Figure 2: Comparison of experimental (discrete points) and model (smooth curves) results for a) Phenylethylamine, b) Styrene, c) Phenylethanol, and d) N-Phenylethyl-9-Octadecenamide for binary mixture with ethyl oleate to phenylalanine molar ratios of \bullet 0.2 : 1.0, \blacklozenge 1.0 : 1.0, and \blacktriangle 5.0 : 1.0, at 350 °C and different batch holding times.

Possible Reactions Pathways for Formation of Amides

