Electronic Supplementary Material (ESI) for Organic and Biomolecular Chemistry
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Supporting Information

Intramolecular Catalysis in the Hydrolysis of Alkyl Monoesters of 1,8-Naphthalic Acid

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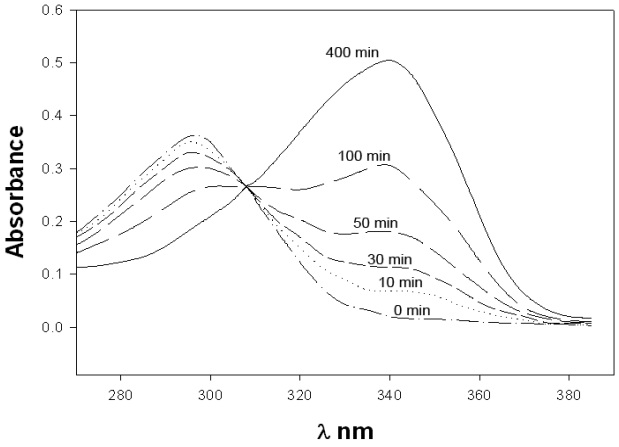

Figure S1 – Absorption spectra as a function of time for the hydrolysis of the isopropyl monoester of 1,8-naphthalic acid (**1b**) 1.9 x 10^{-5} M, at pH 2 and 50 °C. Similar spectral changes are observed in the hydrolysis of all four monoalkyl esters of 1,8-naphthalic acids **1a-d**.

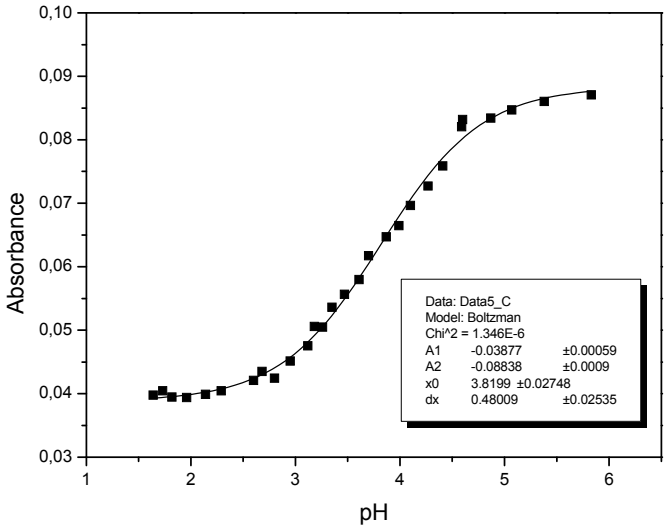

Figure S2 – Absorption as a function of pH for the methyl monoester of 1,8-naphthalic acid (**1b**) 1.9 x 10^{-5} M, at 25.0 °C, λ=263 nm.

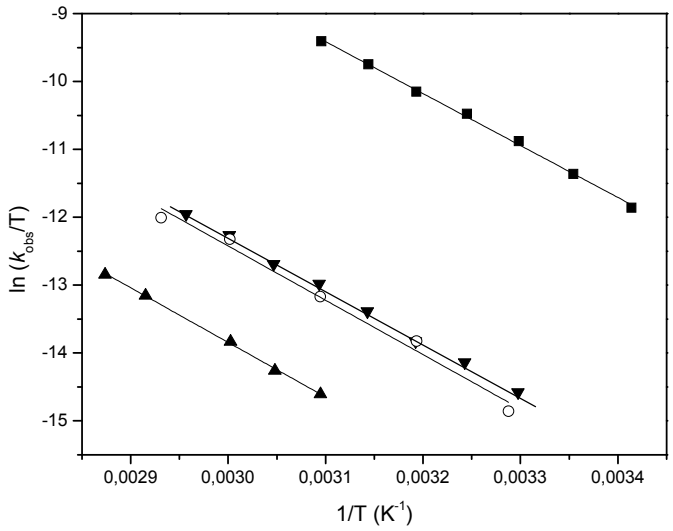

Figure S3 – Eyring plots for hydrolysis of **1a** (■) at pH 0 and for **1b** (▲), **1c** (○) and **1d** (▼) at pH 2.00.

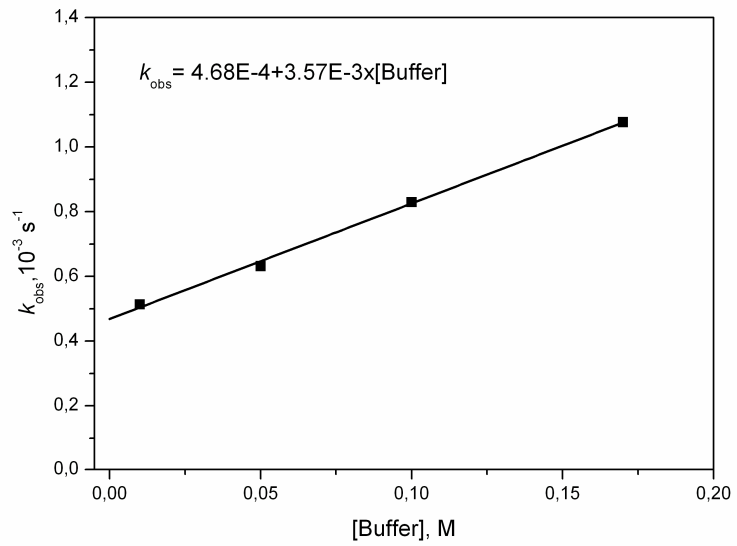

Figure S4 – Observed rate constants for hydrolysis of methyl monoester of 1,8-naphthalic acid as a function of total buffer concentration at pH 3.40, 50 °C. [Buffer] = [chloroacetic acid] + [sodium chloroacetate].

1c.H_2O

C	-0.799124	-1.232070	-0.176904
C	-1.108714	0.162749	-0.030644
C	-0.148519	1.223616	0.113845
C	-0.566757	2.512717	0.407607
C	-1.936234	2.841354	0.496652
C	-2.879611	1.874245	0.241825
C	-2.498559	0.531522	-0.031783
C	1.286080	1.053781	-0.254028
H	0.180807	3.290226	0.522452
H	-2.233089	3.862141	0.719894
H	-3.938965	2.120519	0.246573
C	-1.800732	-2.140641	-0.479957
C	0.529510	-1.858223	0.117071
H	-1.525849	-3.182818	-0.609522
C	-3.152994	-1.749581	-0.569718
C	-3.495548	-0.443590	-0.308786
H	-3.915217	-2.488266	-0.800881
H	-4.537598	-0.132320	-0.313910
O	0.970263	-2.840557	-0.444788
O	1.132694	-1.284753	1.185976
O	2.117469	1.861924	0.419146
O	1.668786	0.306715	-1.150984
H	3.028801	1.758234	0.036906
C	2.392551	-1.858976	1.573311
H	2.728352	-1.268737	2.426532
H	2.262266	-2.907446	1.854601
H	3.107092	-1.793764	0.748117
O	4.272759	1.203671	-1.132755
H	5.047289	0.651850	-0.949140
H	3.572259	0.612955	-1.485327

Zero-point correction= 0.229982 (Hartree/Particle)
Thermal correction to Energy= 0.246964
Thermal correction to Enthalpy= 0.247908
Thermal correction to Gibbs Free Energy= 0.185145
Sum of electronic and zero-point Energies= -878.567681
Sum of electronic and thermal Energies= -878.550700
Sum of electronic and thermal Enthalpies= -878.549756
Sum of electronic and thermal Free Energies= -878.612518
Counterpoise: BSSE energy = 0.002442594646
DeltaG (solv) (kcal/mol) = 2.56

IT.H_2O

C	-0.895753	1.343860	-0.003710
C	-1.130022	-0.055769	-0.116567
C	-0.056712	-0.953984	-0.349637
C	-0.305153	-2.294727	-0.556096
C	-1.631966	-2.790961	-0.498365
C	-2.685130	-1.947352	-0.215438
C	-2.464177	-0.556456	-0.017158
C	1.339084	-0.384635	-0.247057
H	0.521067	-2.968559	-0.758846
H	-1.811360	-3.849378	-0.666146
H	-3.699202	-2.334545	-0.148563
C	-1.941334	2.207457	0.272695
C	0.450576	1.889093	-0.307937
H	-1.740209	3.271994	0.341593
C	-3.253406	1.707927	0.427696
C	-3.511900	0.360094	0.268522
H	-4.065122	2.395787	0.647152
H	-4.528529	-0.016687	0.356342
O	1.763233	-0.251330	1.118202
O	2.225855	-1.117212	-0.988587
C	1.863410	-1.460637	1.878233
O	0.731837	3.066928	-0.330136
O	1.402082	0.978893	-0.695875
H	2.316346	-1.172340	2.829028
H	0.874584	-1.895219	2.063756
H	2.502387	-2.193299	1.372874
H	3.114426	-0.695637	-0.872997
H	3.734026	0.633818	0.595409
O	4.353343	0.468462	-0.140056
H	4.305691	1.274676	-0.679081

Zero-point correction= 0.230648 (Hartree/Particle)
Thermal correction to Energy= 0.246877
Thermal correction to Enthalpy= 0.247822
Thermal correction to Gibbs Free Energy= 0.186979
Sum of electronic and zero-point Energies= -878.552739
Sum of electronic and thermal Energies= -878.536510
Sum of electronic and thermal Enthalpies= -878.535566
Sum of electronic and thermal Free Energies= -878.596408
Counterpoise: BSSE energy = 0.002868023574

DeltaG (solv) (kcal/mol) = 2.64

TS1

C	-0.156547	-1.158775	-0.072106
C	-1.108431	-0.087264	-0.033189
C	-0.763549	1.305658	-0.025694
C	-1.760035	2.255965	0.112328
C	-3.122198	1.893647	0.197019
C	-3.484861	0.569322	0.095926
C	-2.498675	-0.446527	-0.032595
C	0.635659	1.812305	-0.312135
C	-0.559297	-2.470181	-0.244708
C	1.282667	-0.932115	0.223509
C	-1.931566	-2.800886	-0.313849
C	-2.877046	-1.810764	-0.174753
O	2.211254	-1.558057	-0.393022
O	1.469837	-0.443654	1.447921
O	0.935333	2.991526	-0.154295
O	1.439043	0.894626	-0.793931
C	2.816011	-0.228602	1.919189
H	-1.464786	3.300604	0.115012
H	-3.880114	2.665392	0.301543
H	-4.533155	0.279180	0.105440
H	0.191540	-3.253558	-0.290798
H	-2.229824	-3.837530	-0.442511
H	-3.936542	-2.056900	-0.182258
H	3.067558	-0.837233	-0.849118
H	2.711640	-0.018958	2.983305
H	3.423786	-1.122047	1.758016
H	3.250481	0.633280	1.406817
O	3.678738	0.122181	-1.295911
H	3.841342	0.013811	-2.248250
H	2.851642	0.770274	-1.176940

Zero-point correction= 0.225080 (Hartree/Particle)
Thermal correction to Energy= 0.240389
Thermal correction to Enthalpy= 0.241333
Thermal correction to Gibbs Free Energy= 0.182724
Sum of electronic and zero-point Energies= -878.528986
Sum of electronic and thermal Energies= -878.513678
Sum of electronic and thermal Enthalpies= -878.512734
Sum of electronic and thermal Free Energies= -878.571343

DeltaG (solv) (kcal/mol) = -1.64

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TS2

C	-0.913945	1.323307	-0.068876
C	-1.088281	-0.084495	-0.166882
C	0.010304	-0.931037	-0.464140
C	-0.176531	-2.288404	-0.628394
C	-1.466250	-2.851874	-0.470515
C	-2.542531	-2.056150	-0.135568
C	-2.384829	-0.651744	0.025868
C	1.366442	-0.315125	-0.534739
H	0.674644	-2.914122	-0.877711
H	-1.601064	-3.921410	-0.605956
H	-3.528447	-2.493930	0.002850
C	-1.983664	2.137050	0.263567
C	0.394870	1.928237	-0.415772
H	-1.829695	3.209897	0.324330
C	-3.258936	1.575623	0.494135
C	-3.458808	0.214416	0.365017
H	-4.089597	2.225249	0.755168
H	-4.447831	-0.211089	0.519742
O	1.812672	-0.049733	1.138866
O	2.330135	-0.956959	-1.082105
C	1.768571	-1.206973	1.974475
O	0.633905	3.114487	-0.407980
O	1.368247	1.066493	-0.871676
H	0.730945	-1.445992	2.227867
H	2.235021	-2.071207	1.482439
H	2.317670	-0.978479	2.894107
H	3.415594	-0.367375	-0.611334
H	3.056388	0.214851	0.834115
O	4.014631	0.189047	0.192358
H	4.191170	1.089932	-0.130379

Zero-point correction= 0.224643 (Hartree/Particle)
Thermal correction to Energy= 0.239538
Thermal correction to Enthalpy= 0.240482
Thermal correction to Gibbs Free Energy= 0.183035
Sum of electronic and zero-point Energies= -878.522459
Sum of electronic and thermal Energies= -878.507565
Sum of electronic and thermal Enthalpies= -878.506620
Sum of electronic and thermal Free Energies= -878.564068

DeltaG (solv) (kcal/mol) = 1.57

NA

C	-0.417041	2.434001	-0.000129
C	-1.828514	2.438056	-0.000258
C	-2.531419	1.248344	-0.000114
C	-1.852973	0.000068	0.000027
C	-0.424153	0.000015	-0.000042
C	0.276432	1.234240	-0.000086
C	-2.531512	-1.248172	0.000190
C	-1.828708	-2.437930	0.000252
C	-0.417222	-2.433993	0.000097
C	0.276339	-1.234286	-0.000041
C	1.754798	1.236620	0.000155
C	1.754679	-1.236805	-0.000258
O	2.387908	-0.000049	-0.001188
O	2.449311	2.223120	0.001060
O	2.449218	-2.223236	0.000262
H	0.141708	3.364622	-0.000125
H	-2.360364	3.385014	-0.000414
H	-3.618891	1.254769	-0.000063
H	-3.618985	-1.254521	0.000291
H	-2.360631	-3.384847	0.000364
H	0.141427	-3.364669	0.000114

Zero-point correction= 0.150450 (Hartree/Particle)
Thermal correction to Energy= 0.160595
Thermal correction to Enthalpy= 0.161540
Thermal correction to Gibbs Free Energy= 0.114367
Sum of electronic and zero-point Energies= -686.475418
Sum of electronic and thermal Energies= -686.465273
Sum of electronic and thermal Enthalpies= -686.464329
Sum of electronic and thermal Free Energies= -686.511502

DeltaG (solv) (kcal/mol) = -2.59

MeOH

O	-0.749278	0.122886	-0.000014
C	0.668428	-0.020868	-0.000026
H	-1.156340	-0.756196	0.000227
H	1.029450	-0.548483	-0.894695
H	1.029856	-0.544244	0.897071
H	1.080689	0.991041	-0.002338

Zero-point correction= 0.051301 (Hartree/Particle)
Thermal correction to Energy= 0.054620
Thermal correction to Enthalpy= 0.055565
Thermal correction to Gibbs Free Energy= 0.028550
Sum of electronic and zero-point Energies= -115.673892
Sum of electronic and thermal Energies= -115.670573
Sum of electronic and thermal Enthalpies= -115.669628
Sum of electronic and thermal Free Energies= -115.696643

DeltaG (solv) (kcal/mol) = -1.26

H_2O

O	0.000000	0.000000	0.117418
H	0.000000	0.771019	-0.469672
H	0.000000	-0.771019	-0.469672

Zero-point correction= 0.021088 (Hartree/Particle)
Thermal correction to Energy= 0.023923
Thermal correction to Enthalpy= 0.024867
Thermal correction to Gibbs Free Energy= 0.003426
Sum of electronic and zero-point Energies= -76.401485
Sum of electronic and thermal Energies= -76.398650
Sum of electronic and thermal Enthalpies= -76.397705
Sum of electronic and thermal Free Energies= -76.419146

DeltaG (solv) (kcal/mol) = -4.40

HPLC analysis:

All compounds were characterized in solution prior to the kinetic experiments in a Varian ProStar high-performance liquid chromatography equipment using an ultraviolet detector set at 310 nm and a Microsorb-MV C18 reversed-phase column (250 mm x 4.6 mm, 5 µm) at room temperature. In all samples, a volume of 20 µL was injected, with concentration $1x10^{-5}$ M. The analyses were performed with a flow-rate of 1 mL min^{-1}, isocratic elution, using $CH_3CN:H_2O$ 70:30 (v/v) in all cases.

With all samples the only significant impurity is the starting material naphthalic anhydride (NA). NA does not interfere with the kinetic analysis, since it is the reaction product in all cases.

Using the UV detector set at 310 nm allows directed determination of the naphthalic monoester to NA ratio since this wavelength corresponds to the isosbestic point for the cyclization of naphthalic esters to NA.

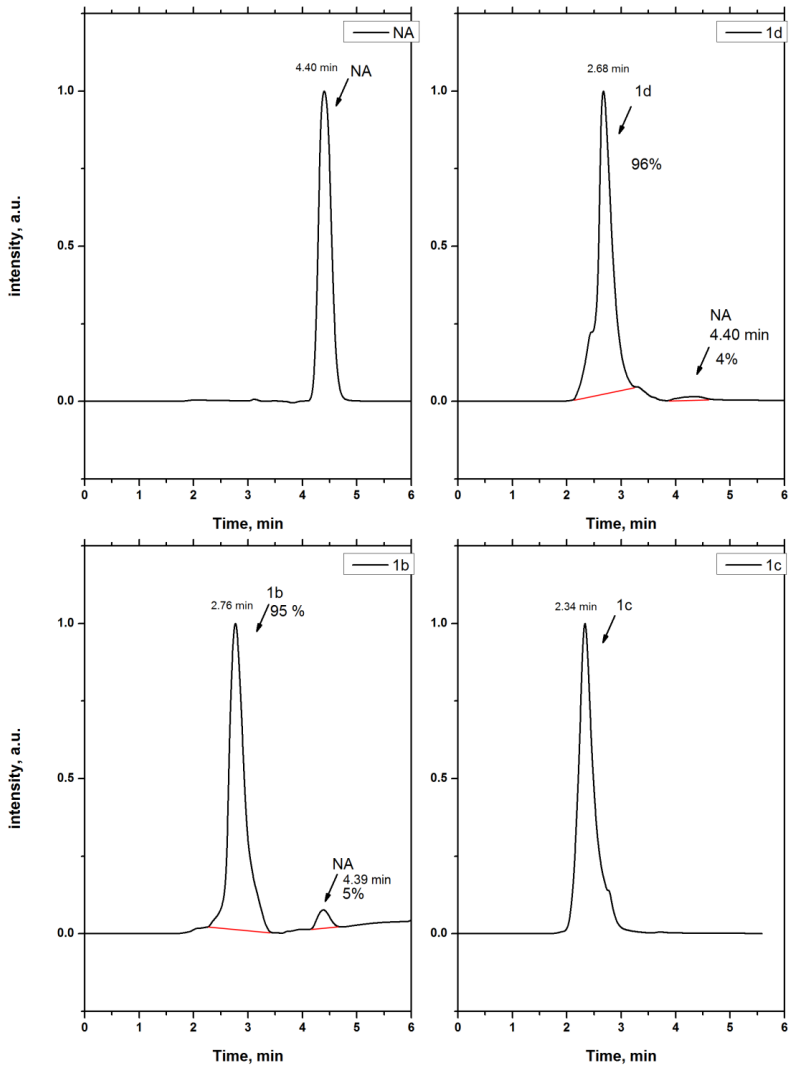

Figure S5 HPLC of a $1x10^{-5}$ M solution of naphthalic anhydride (**NA**) and of the isopropyl (**1b**), methyl (**1c**) and *n*-butyl (**1d**) monoesters of 1,8-naphthalic acid.