CHEMISTRY
A EUROPEAN JOURNAL

Supporting Information

“Steric Effects in the Uncatalyzed and DMAP-Catalyzed Acylation of Alcohols - Quantifying the Window of Opportunity in Kinetic Resolution Experiments “

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Experimental Details

Solvent:

Dichloromethane was vigorously stirred over concentrated H_2SO_4 (for at least three days) to remove traces of olefins. Afterwards it was shaken two or three times more with adequate portions of concentrated H_2SO_4 until the acid layer remained colorless. The organic layer was then washed with water, 5% aqueous $NaHCO_3$ solution and water. The dichloromethane layer was then pre-dried (at least for two days) over $CaCl_2$ and afterwards distilled from CaH_2. The solvent was always redistilled in a circulation apparatus from CaH_2 under a nitrogen atmosphere for at least two hours before it was utilized for kinetic measurements.

Chemicals:

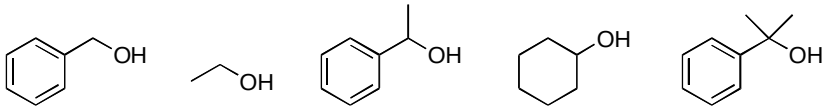
4-Dimethylaminopyridine (DMAP) was purchased from Fluka Chemical Company Ltd. and used without further purification. Cyclohexanol (Merck-VWR-international) and *n*-nonane (used as internal standard, Acros Organics) were stirred for several hours over sodium and afterwards distilled off. Triethylamine was distilled from CaH_2 under nitrogen. Acetic anhydride was refluxed with coarse Mg fillings at 80-90 °C for five days and distilled. Ethanol was purchased in absolute quality, refluxed for one hour over sodium together with phtalic acid diethyl ester, distilled and stored over dry molecular sieves 4Å under a nitrogen atmosphere. Bn-OH, *dl*-PhCHMe-OH (Acros Organics) and $PhCMe_2$-OH (Acros Organics) were purified by fractional distillation under reduced pressure and stored under a nitrogen atmosphere. The propionic, iso-butyric, iso-valeric and pivalic anhydride were purchased either from Acros Organics or Fluka Chemical Company Ltd., stirred with P_2O_5 for roughly one hour (for propionic anhydride stirring over P_2O_5 for at least three hours is more suitable) and then fractionally distilled under reduced pressure and stored under a nitrogen atmosphere.

Equipment

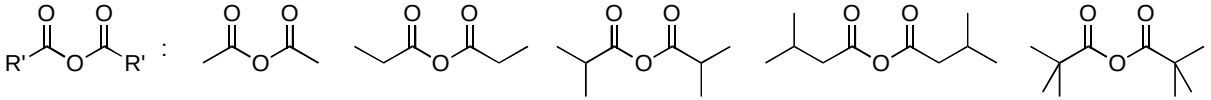
Kinetic measurements have been performed under a nitrogen atmosphere at 20 ^{o}C. All kinetic measurements have been conducted using gas chromatography (FISONS 8130, Column: SE30) with a FID detection system.

Substrates

R−OH :



3a **3b** **3c** **3d** **3e**



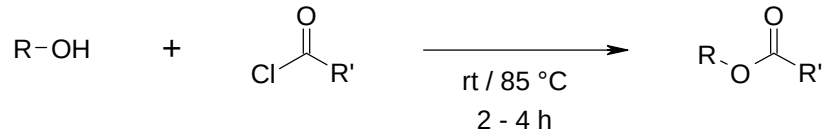
4a **4b** **4c** **4d** **4e**

Kinetic Measurements:

Reaction solutions were prepared through mixing three types of freshly arranged stock solutions with exact concentrations of catalyst containing $6*10^{-3}$ mol l^{-1} DMAP (AA) - of alcohols containing $60*10^{-3}$ mol l^{-1} R-OH (AB-AX), $60*10^{-3}$ mol l^{-1} *n*-nonane (AC) and $180*10^{-3}$ mol l^{-1} triethylamine (AD) - and anhydrides (BA-BB) containing $360*10^{-3}$ mol l^{-1} exclusively of appropriate $(RCO)_2O$ each in CH_2Cl_2 as solvent. Variation of catalyst concentrations is achieved through dilution with pure CH_2Cl_2. Variation of triethylamine ratios is made by enhancing the quantities of absolute amine concentration in stock solutions to $240*10^{-3}$ mol l^{-1} (4 eq) and $360*10^{-3}$ mol l^{-1} (6 eq) respectively. The three separate solutions are mixed together in equal shares of 200 µl each in a 2 ml brown glass vial equipped with a septum immediately prior to use, whereas the catalyst solution is finally inserted and activates the corresponding kinetic run. Reactions have been performed under a nitrogen atmosphere at 20 °C. All kinetic measurements were recorded using gas chromatography (FISONS 8130, Column: SE30) with *n*-nonane as internal standard. Right after catalyst injection the closed vials were carefully shaken and the initial measurement was taken. Monitoring the disappearance of the minor reaction component (R-OH) under pseudo-first order conditions at several time intervals by injecting 5 µl aliquots of the reaction samples into the gas chromatograph provides the rate constant. For the comparative slow reactions conducted for the pivalic anhydride a different detection method was maintained. The ongoing reaction was monitored by the appearance of the corresponding ester product according to *n*-nonane as internal standard, since the effect in the ratios of alcohol to *n*-nonane was to marginal. Every kinetic run was conducted at least two times, except for the iso-valeric anhydride because of its extremely olfactory properties. The kinetic run for the reaction of benzyl alcohol and iso-butyric anhydride was performed in triplicate as well as the corresponding non catalyzed background reactions.

Synthesis of ester products

Some of the esterified alcohols have been synthesized independently using the solvent free procedure of Ranu *et al.* [1]. The general synthetic route used for our purpose is displayed in scheme 1. The typical procedure needs just a neat mixture of alcohol and an acid anhydride, room temperature or heating to 80-85 °C, neither solvent nor catalyst and 2 – 4 hours to complete the reaction. Using bulky compounds e. g. pivalic acid chloride exceeding reaction times would be more acceptable for higher product yields.



Scheme 1: General synthetic route for synthesizing esters under solvent free conditions according to the procedure of Ranu *et al*.[1].

General procedure for the acylation reactions:

A neat mixture of freshly destilled cyclohexanol (10 mmol) and the appropriate acid chloride (12 mmol, insertion of chloride should be slow in some cases; can cause a gently warming up and frothing up of the reaction mixture) was stirred in a 25 ml two-necked round-bottomed flask for 2-4 hours without any solvent and catalyst under a nitrogen atmosphere at room temperature. After completed reaction time the product mixture was extracted with 20 ml diethyl ether. The organic extract was neutralized with an excess of 25 ml saturated aqueous $NaHCO_3$ solution and washed again with 25 ml of aqueous $NaHCO_3$ solution (5%), 25 ml saturated brine and dried with Na_2SO_4. After evaporating the organic solvent the crude product if not pure enough for standard analysis can purified by short column chromatography over silica gel with chloroform. In the case of pivalic acid chloride the reaction was heated to 85 °C for 4 hours before the general work up was conducted.

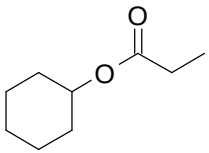
Chemicals:

The propionic-, iso-butyric-, iso-valeric- and pivalic acid chlorides were either purchased from Fluka Chemical Company Ltd., Acros Organics or Sigma-Aldrich and used without further purification. Cyclohexanol (Merck-VWR-international) was stirred for several hours over sodium and afterwards distilled off. The ester products not mentioned here where either commercially available or already synthesized (e.g. cyclohexyl propionate and other acetates) by the procedure given by Ranu *et al*.[1].

Analysis:

NMR spectra were recorded on a Bruker AMX 300 spectrometer [300.13 MHz (^{1}H) and 75.47 MHz (^{13}C)]. Chemical shifts are given as δ values in ppm relative to $CDCl_3$ = 7.24 (^{1}H) and $CDCl_3$ = 77.0 (^{13}C) as the internal standard and J values in Hz. Mass spectra were recorded by GC-MS with an Agilent 6890 Network GC-system equipped with a Agilent 7683 Series Injector and a Agilent 5973 Network Mass Selective Detector (all parts by Agilent Technologies). The IR spectra were measured with a Perkin-Elmer Spectrum BX FT-IR System.

Cyclohexyl propionate / propionic acid cyclohexyl ester:



According to the general procedure a colorless and crystal clear liquid was received after 2.5 h at room temperature. Yield: 1.446 g (93%)

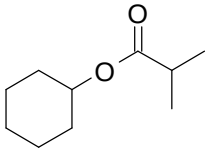
^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.67 (m, 1 H), 2.21 (q, 2 H, J = 7.6 Hz), 1.78 – 1.22 (m, 10 H), 1.04 (t, 3 H, J = 7.6 Hz).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 174.4 (C=O), 72.8 (C-O), 32.2 (CH_2), 28.5 (CH_2), 26.0 (CH_2), 24.3 (CH_2), 9.7 (CH_3).

GC-MS *m/z* 157 [MH^+], 127, 113, 99, 83, 82, 81, 75, 67, 57, 55, 41.

IR (cm^{-1}): 2936 (s), 2859, 1730 (s), 1451, 1378, 1356, 1274, 1186 (s), 1124, 1081, 1038, 1019, 945, 926, 908, 868, 842, 807.

Cyclohexyl *i*-butyrate / isobutyric acid cyclohexyl ester:



According to the general procedure a colorless and crystal clear liquid was received after 1.5 h at room temperature. Yield: 1.481 g (87%)

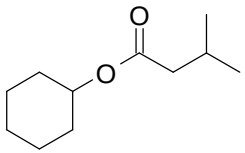
^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.70 (m, 1 H), 2.46 (sept, 1 H, J = 7.2 Hz), 1.84 – 1.21 (m, 10 H), 1.11 (d, 6 H, J = 7 Hz).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 177.7 (C=O), 72.6 (C-O), 34.9 (CH), 32.2 (CH_2), 26.1 (CH_2), 24.3 (CH_2), 19.6 (CH_3).

GC-MS *m/z* 171 [MH^+], 127, 89, 83, 71, 55, 43.

IR (cm^{-1}): 2973, 2935 (s), 2860, 1728 (s), 1470, 1451, 1387, 1342, 1259, 1191, 1160, 1124, 1096, 1071, 1039, 1017, 961, 911, 893, 840.

Cyclohexyl isovalerate / isovaleric acid cyclohexyl ester / 3 methyl-butyric acid cyclohexyl ester:



According to the general procedure a colorless and clear liquid was received after 2 h at room temperature. Yield: 1.695 g (92 %)

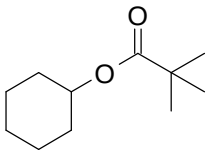
^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.74 (m, 1 H), 2.15 – 2.00 (m, 1 H), 2.13 (d, 2 H, J = 6 Hz), 1.84 – 1.12 (m, 10 H), 0.93 (d, 6 H, J = 6 Hz).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 173.3 (C=O), 72.9 (C-O), 44.6 (CH_2), 32.4 (CH_2), 26.5 (CH), 26.1 (CH_2), 24.4 (CH_2), 23.0 (CH_3).

GC-MS *m/z* 185 [MH^+], 141, 103, 87, 85, 82, 67, 57.

IR (cm^{-1}): 2935 (s), 2860, 1728 (s), 1450, 1360, 1292, 1255, 1187, 1120, 1094, 1040, 1018, 982.

Cyclohexylpivalat / 2,2-dimethyl-propionic acid cyclohexyl ester:



According to the general procedure a nearly colorless and clear liquid was received after 4 h heating to 85 °C. Yield: 0.903 g (49 %)

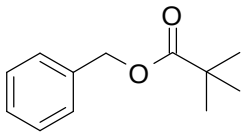
^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.71 (m, 1 H), 1.79 – 1.27 (m, 10 H), 1.14 (s, 9 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 178.5 (C=O), 72.4 (C-O), 39.3 (C_q), 32.0 (CH_2), 27.8 (CH_3), 26.1 (CH_2), 24.1 (CH_2).

GC-MS *m/z* 185 [MH^+], 127, 103, 83, 67, 57, 55, 41.

IR (cm^{-1}): 2935 (s), 2861, 1724 (s), 1480, 1451, 1396, 1364, 1283, 1163 (s), 1150, 1123, 1041, 1016, 931, 902, 771.

Benzyl pivalate / 2,2-dimethyl-propionic acid benzyl ester:



According to the general procedure a nearly colorless and clear liquid was received after 2 h at room temperature. Yield: 1.769 g (92 %)

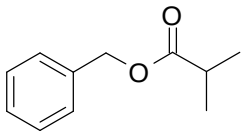
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30 – 7.19 (m, 5 H), 5.05 (s, 2 H), 1.18 (s, 9 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 178.7 (C=O), 137.0 (C_q), 129.0 (CH, B), 128.5 (CH, C), 128.2 (CH, A), 66.5 (CH_2), 39.3 (C_q), 27.7 (CH_3).

GC-MS *m/z* 192 [M^+], 108, 91, 85, 77, 65, 57, 51, 41.

IR (cm^{-1}): 3034, 2973, 2873, 1727 (s), 1498, 1480, 1456, 1397, 1365, 1280, 1139 (s), 1030, 966, 856, 770, 733, 695.

Isobutyric acid benzyl ester:



According to the general procedure a nearly colorless and clear liquid was received after 1.5 h at room temperature. Yield:1.706 g (96 %)

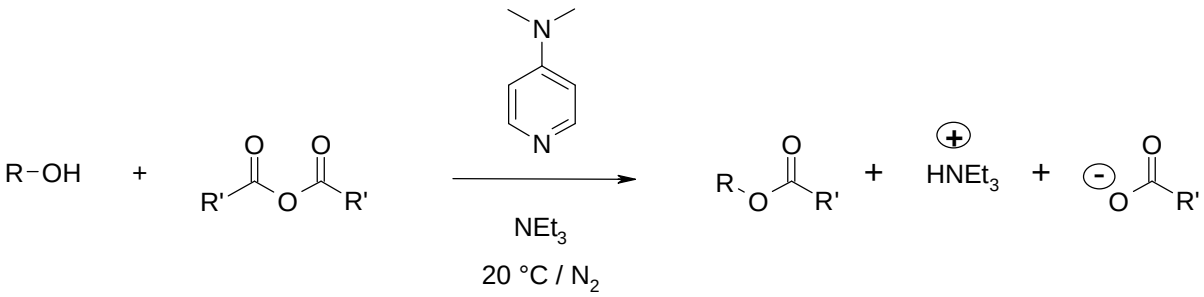
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37 – 7.32 (m, 5 H), 5.12 (s, 2 H), (sept., 1 H, J = 7 Hz) 1.20 (d, 6 H, J = 7 Hz).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 176.8 (C=O), 136.25 (C_q), 128.5 (CH, B), 128.0 (CH, C), 127.9 (CH, A), 66.0 (CH_2), 34.0 (CH), 18.9 (CH_3).

GC-MS *m/z* 178 [M^+], 108, 91, 77, 71, 65, 57, 51.

IR (cm^{-1}): 3067, 3034, 2974, 2938, 2877, 1732 (s), 1498, 1470, 1456, 1388, 1343, 1258, 1188, 1147 (s), 1098, 1070, 1030, 966, 930, 905, 868, 815, 748, 696.

Data summary for the kinetic measurements



Scheme 2: General reaction outline for the kinetic measurements.

The rate law for DMAP-catalyzed acylation is composed as follows:

$$r = k_2[\text{R-OH}][(RCO)_2O] + k_3[\text{R-OH}][(RCO)_2O][\text{DMAP}]$$

The rate constant for pseudo-first order conditions $k_{1\Psi}$ results from the above expression as:

$$k_{1\Psi} = k_3[(RCO)_2O]_0[\text{DMAP}]_0 + k_2[(RCO)_2O]_0$$

Definition for the catalytic efficiency as the catalyzed part at a given DMAP concentration over the uncatalyzed term for the occurring background reaction:

$$k_3[DMAP]_{1mM}/k_2$$

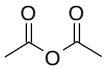
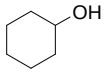
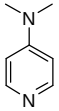
Supplemental Table 1. Rate constants k_2 (in M^{-1} s^{-1}) and k_3 (in M^{-2} s^{-1} in the acylation of alcohols **3s** - **3e** with anhydrides **4a** - **4e** in CH_2Cl_2 at 20 ^oC.[a]

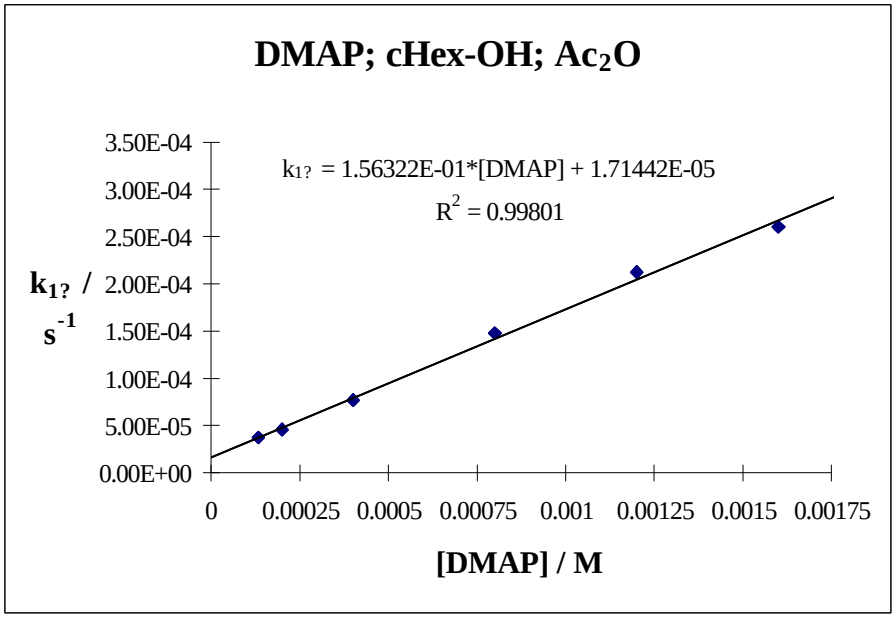
alcohol	anyhdride	k_2 (M^{-1} s^{-1})	k_3 (M^{-2} s^{-1})	[alcohol] (M)	[anhydride] (M)	[NEt3] (M)	[DMAP] (M)
3a	**4a**	1.77±0.06 x 10^{-3}	4.06±0.03 x 10^{+1}	0.005	0.03	0.015	0.0001 - 0.0003
3b	**4a**	7.93±0.45 x 10^{-4}	1.35±0.01 x 10^{+1}	0.01	0.06	0.03	0.0001 - 0.0005
3c	**4a**	6.07±0.28 x 10^{-4}	2.80±0.04	0.015	0.09	0.045	0.0002 - 0.0012
3d	**4a**	1.43±0.20 x 10^{-4}	1.30±0.02	0.02	0.12	0.06	0.00013 - 0.0016
3e	**4a**	8.74±0.41 x 10^{-6}	3.22±0.06 x 10^{-2}	0.02	0.12	0.06	0.0002 - 0.001
3d	**4b**	2.80±0.67 x 10^{-5}	7.36±0.09 x 10^{-1}	0.02	0.12	0.06	0.0001 - 0.00125
3d	**4c**	1.08±0.20 x 10^{-5}	4.62±0.03 x 10^{-1}	0.02	0.12	0.06	0.0001 - 0.00125
3d	**4d**	1.27±0.18 x 10^{-5}	1.56±0.02 x 10^{-1}	0.02	0.12	0.06	0.0001 - 0.00125
3d	**4e**	2.72±0.02 x 10^{-7}	1.62±0.03 x 10^{-4}	0.02	0.12	0.06	0.0001 - 0.00125
3a	**4e**	2.04±0.03 x	6.02±0.04 x	0.02	0.12	0.06	0.0001 -

		10^{-6}	10^{-3}				0.00125
3a	**4c**	1.51±0.41 x 10^{-5}	1.99±0.01 x 10^{+1}	0.02	0.12	0.06	0.0 - 0.000125

[a] numbering according to the manuscript.

Supplemental Table 2: Rate Data for the transfer reaction of acetic anhydride and cyclohexanol in CH_2Cl_2 at 20 °C in the presence of DMAP as catalyst and triethylamine as auxiliary base (component ratio: alcohol/amine/anhydride = 1:3:6).

 / M	 / M	 / M	 / M	conversion / %	$k_{1?}$ / s^{-1}
0.12	0.02	0.06	0.000133	50.8	3.853E-05
0.12	0.02	0.06	0.0002	54.9	4.520E-05
0.12	0.02	0.06	0.0004	55.5	7.643E-05
0.12	0.02	0.06	0.0008	52.2	1.478E-04
0.12	0.02	0.06	0.0012	66.0	2.125E-04
0.12	0.02	0.06	0.0016	36.7	2.598E-04



Supplemental Figure 2: Dependence of $k_{1\Psi}$ on the varying concentration of DMAP with $[Ac_2O]_0$ = 0.12 M, [cyclohexanol]$_0$ = 0.02 M, $[NEt_3]_0$ = 0.06 M.

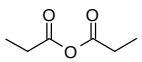
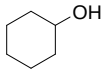
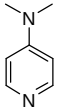
Results:

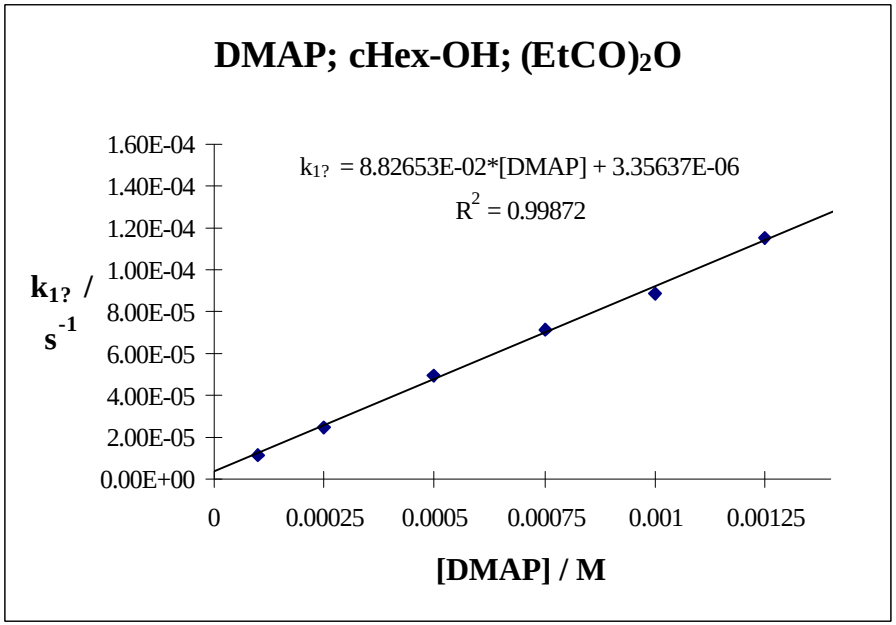
$k_2*[(RCO)_2O]_0 = 1.714 \pm 0.237 \times 10^{-5}\ s^{-1}$ => $k_2 = 1.429 \pm 0.198 \times 10^{-4}\ M^{-1}\ s^{-1}$

$k_3*[(RCO)_2O]_0 = 1.563 \pm 0.026 \times 10^{-1}\ M^{-1}\ s^{-1}$ => $k_3 = 1.303 \pm 0.022\ 10^{0}\ M^{-2}\ s^{-1}$

catalytic efficiency: $k_3*0.001/k_2$ = **9.118**

Supplemental Table 3: Rate Data for the transfer reaction of propionic anhydride and cyclohexanol in CH_2Cl_2 at 20 °C in the presence of DMAP as catalyst and triethylamine as auxiliary base (component ratio: alcohol/amine/anhydride = 1:3:6).

 / M	 / M	 / M	 / M	conversion / %	$k_{1?}$ / s^{-1}
0.12	0.02	0.06	0.0001	35.1	1.163E-05
0.12	0.02	0.06	0.00025	70.7	2.474E-05
0.12	0.02	0.06	0.0005	67.3	4.914E-05
0.12	0.02	0.06	0.00075	73.2	7.140E-05
0.12	0.02	0.06	0.001	68.4	8.825E-05
0.12	0.02	0.06	0.00125	72.4	1.148E-04



Supplemental Figure 3: Dependence of $k_{1\Psi}$ on the varying concentration of DMAP with $[(EtCO)_2O]_0$ = 0.12 M, $[cyclohexanol]_0$ = 0.02 M, $[NEt_3]_0$ = 0.06 M.

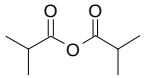
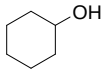
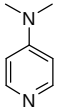
Results:

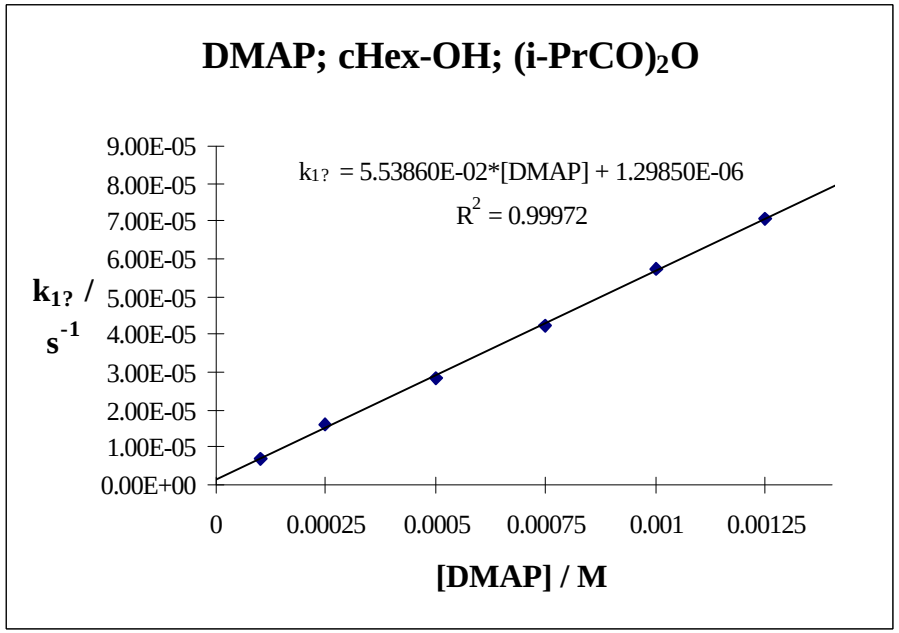
$k_2*[(RCO)_2O]_0 = 3.356 \pm 0.806 \times 10^{-6}\ s^{-1}$ => $k_2 = 2.797 \pm 0.672 \times 10^{-5}\ M^{-1}\ s^{-1}$

$k_3*[(RCO)_2O]_0 = 8.827 \pm 0.106 \times 10^{-2}\ M^{-1}\ s^{-1}$ => $k_3 = 7.355 \pm 0.089\ 10^{-1}\ M^{-2}\ s^{-1}$

catalytic efficiency: $k_3*0.001/k_2$ = **26.298**

Supplemental Table 4: Rate Data for the transfer reaction of iso-butyric anhydride and cyclohexanol in CH_2Cl_2 at 20 °C in the presence of DMAP as catalyst and triethylamine as auxiliary base (component ratio: alcohol/amine/anhydride = 1:3:6).

 / M	 / M	 / M	 / M	conversion / %	$k_{1?}$ / s^{-1}
0.12	0.02	0.06	0.0001	72.9	6.805E-06
0.12	0.02	0.06	0.00025	78.1	1.587E-05
0.12	0.02	0.06	0.0005	64.0	2.830E-05
0.12	0.02	0.06	0.00075	75.7	4.221E-05
0.12	0.02	0.06	0.001	64.3	5.724E-05
0.12	0.02	0.06	0.00125	61.9	7.060E-05



Supplemental Figure 4: Dependence of $k_{1\Psi}$ on the varying concentration of DMAP with $[(i\text{-}PrCO)_2O]_0$ = 0.12 M, $[cyclohexanol]_0$ = 0.02 M, $[NEt_3]_0$ = 0.06 M.

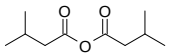
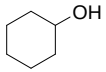
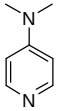
Results:

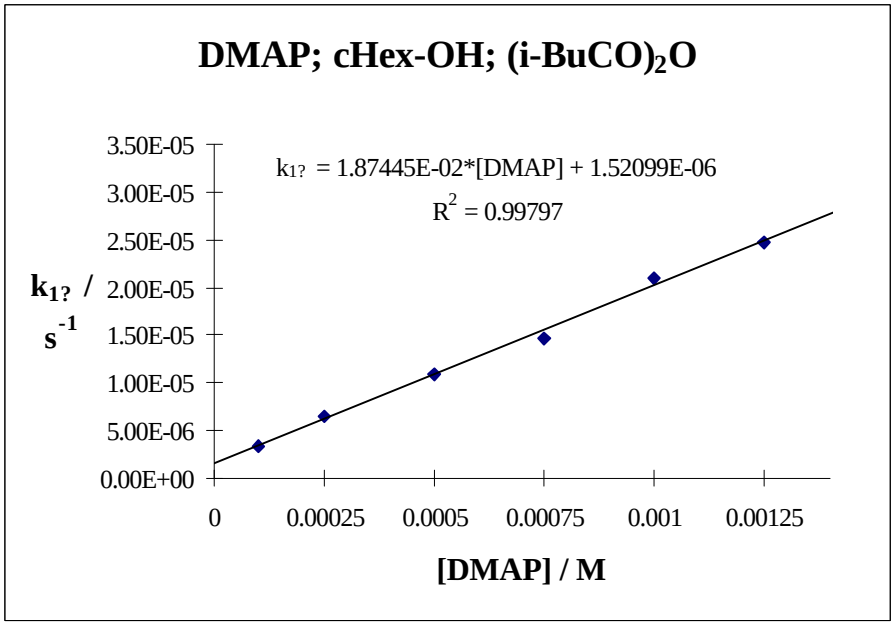
$k_2*[(RCO)_2O]_0 = 1.299 \pm 0.238 \times 10^{-6}\ s^{-1}$ => $k_2 = 1.082 \pm 0.199 \times 10^{-5}\ M^{-1}\ s^{-1}$

$k_3*[(RCO)_2O]_0 = 5.539 \pm 0.031 \times 10^{-2}\ M^{-1}\ s^{-1}$ => $k_3 = 4.616 \pm 0.026\ 10^{-1}\ M^{-2}\ s^{-1}$

catalytic efficiency: $k_3*0.001/k_2$ = **42.654**

Supplemental Table 5: Rate Data for the transfer reaction of iso-valeric anhydride and cyclohexanol in CH_2Cl_2 at 20 °C in the presence of DMAP as catalyst and triethylamine as auxiliary base (component ratio: alcohol/amine/anhydride = 1:3:6).

 / M	 / M	 / M	 / M	conversion / %	$k_{1?}$ / s^{-1}
0.12	0.02	0.06	0.0001	65.5	3.361E-06
0.12	0.02	0.06	0.00025	60.4	6.518E-06
0.12	0.02	0.06	0.0005	62.6	1.086E-05
0.12	0.02	0.06	0.00075	65.4	1.472E-05
0.12	0.02	0.06	0.001	61.2	2.101E-05
0.12	0.02	0.06	0.00125	62.5	2.483E-05



Supplemental Figure 5: Dependence of $k_{1\Psi}$ on the varying concentration of DMAP with $[(i\text{-}BuCO)_2O]_0$ = 0.12 M, $[cyclohexanol]_0$ = 0.02 M, $[NEt_3]_0$ = 0.06 M.

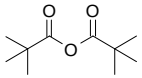
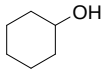
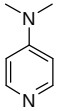
Results:

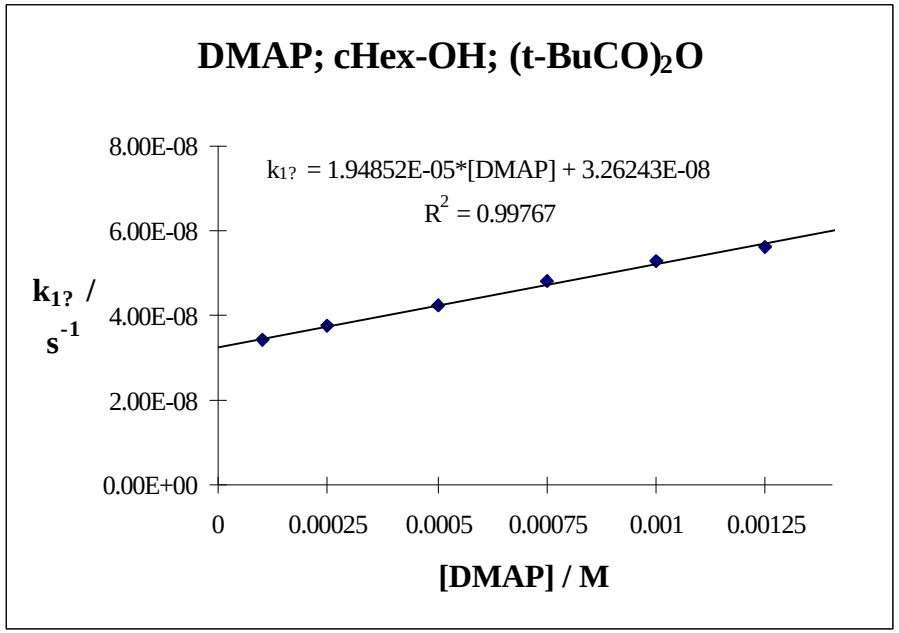
$k_2*[(RCO)_2O]_0 = 1.521 \pm 0.216 \times 10^{-5}\ s^{-1}$ => $k_2 = 1.267 \pm 0.180 \times 10^{-5}\ M^{-1}\ s^{-1}$

$k_3*[(RCO)_2O]_0 = 1.874 \pm 0.028 \times 10^{-2}\ M^{-1}\ s^{-1}$ => $k_3 = 1.562 \pm 0.024\ 10^{-1}\ M^{-2}\ s^{-1}$

catalytic efficiency: $k_3*0.001/k_2$ = **12.324**

Supplemental Table 6: Rate Data for the transfer reaction of pivalic anhydride and cyclohexanol in CH_2Cl_2 at 20 °C in the presence of DMAP as catalyst and triethylamine as auxiliary base (component ratio: alcohol/amine/anhydride = 1:3:6).

 / M	 / M	 / M	 / M	conversion / %	$k_{1?}$ / s^{-1}
0.12	0.02	0.06	0.0001	1.0	3.414E-08
0.12	0.02	0.06	0.00025	1.1	3.743E-08
0.12	0.02	0.06	0.0005	1.2	4.245E-08
0.12	0.02	0.06	0.00075	1.4	4.798E-08
0.12	0.02	0.06	0.001	1.8	5.263E-08
0.12	0.02	0.06	0.00125	2.6	5.613E-08



Supplemental Figure 6: Dependence of $k_{1\Psi}$ on the varying concentration of DMAP with $[(t\text{-}BuCO)_2O]_0$ = 0.12 M, $[cyclohexanol]_0$ = 0.02 M, $[NEt_3]_0$ = 0.06 M.

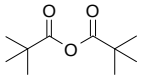
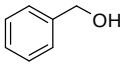
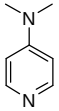
Results:

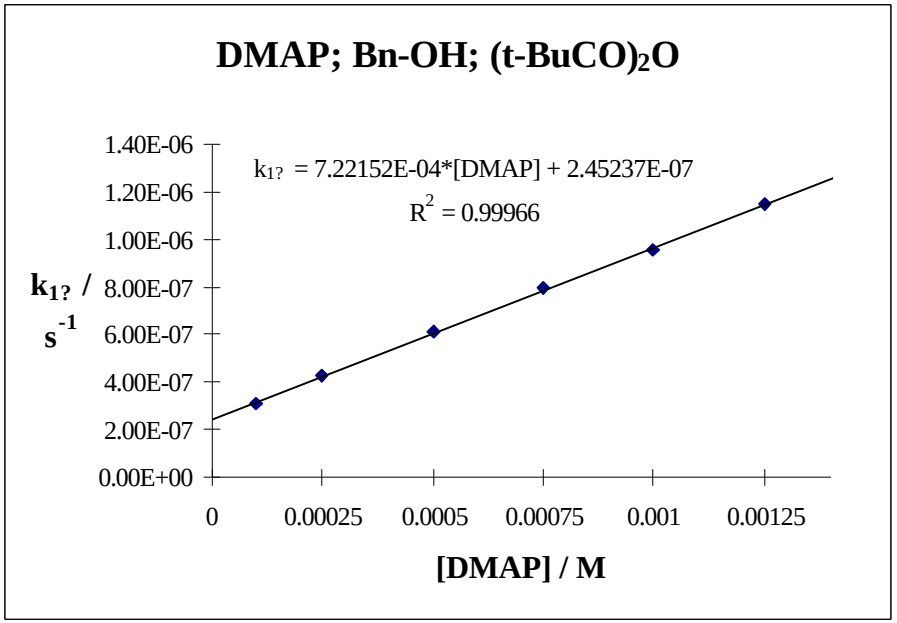
$k_2*[(RCO)_2O]_0 = 3.262 \pm 0.024 \times 10^{-8}\ s^{-1}$ => $k_2 = 2.719 \pm 0.020 \times 10^{-7}\ M^{-1}\ s^{-1}$

$k_3*[(RCO)_2O]_0 = 1.949 \pm 0.032 \times 10^{-5}\ M^{-1}\ s^{-1}$ => $k_3 = 1.624 \pm 0.026\ 10^{-4}\ M^{-2}\ s^{-1}$

catalytic efficiency: $k_3*0.001/k_2$ = **0.597**

Supplemental Table 7: Rate Data for the transfer reaction of pivalic anhydride and Bn-OH in CH_2Cl_2 at 20 °C in the presence of DMAP as catalyst and triethylamine as auxiliary base (component ratio: alcohol/amine/anhydride = 1:3:6).

 / M	 / M	 / M	 / M	conversion / %	$k_{1?}$ / s^{-1}
0.12	0.02	0.06	0.0001	17.3	3.088E-07
0.12	0.02	0.06	0.00025	23.9	4.305E-07
0.12	0.02	0.06	0.0005	31.5	6.110E-07
0.12	0.02	0.06	0.00075	25.8	7.961E-07
0.12	0.02	0.06	0.001	23.4	9.557E-07
0.12	0.02	0.06	0.00125	34.2	1.150E-06



Supplemental Figure 7: Dependence of $k_{1\Psi}$ on the varying concentration of DMAP with $[(t\text{-}BuCO)_2O]_0$ = 0.12 M, $[Bn\text{-}OH]_0$ = 0.02 M, $[NEt_3]_0$ = 0.06 M.

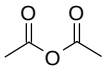
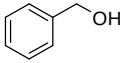
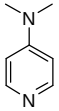
Results:

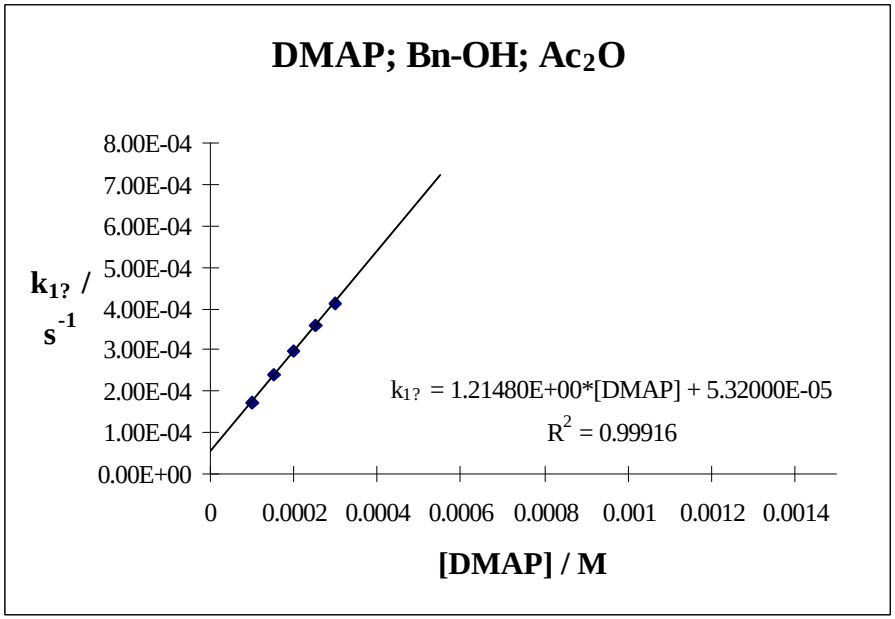
$k_2*[(RCO)_2O]_0 = 2.452 \pm 0.034 \times 10^{-7}\ s^{-1}$ => $k_2 = 2.044 \pm 0.028 \times 10^{-6}\ M^{-1}\ s^{-1}$

$k_3*[(RCO)_2O]_0 = 7.222 \pm 0.045 \times 10^{-4}\ M^{-1}\ s^{-1}$ => $k_3 = 6.018 \pm 0.037\ 10^{-3}\ M^{-2}\ s^{-1}$

catalytic efficiency: $k_3*0.001/k_2$ = **2.945**

Supplemental Table 8: Rate Data for the transfer reaction of acetic anhydride and Bn-OH in CH_2Cl_2 at 20 °C in the presence of DMAP as catalyst and triethylamine as auxiliary base (component ratio: alcohol/amine/anhydride = 1:3:6).

 / M	 / M	 / M	 / M	conversion / %	$k_{1?}$ / s^{-1}
0.03	0.005	0.015	0.0001	71.7	1.704E-04
0.03	0.005	0.015	0.00015	68.6	2.383E-04
0.03	0.005	0.015	0.0002	71.6	2.989E-04
0.03	0.005	0.015	0.00025	73.2	3.599E-04
0.03	0.005	0.015	0.0003	75.6	4.133E-04



Supplemental Figure 8: Dependence of $k_{1\Psi}$ on the varying concentration of DMAP with $[(Ac_2O]_0$ = 0.03 M, $[Bn\text{-}OH]_0$ = 0.005 M, $[NEt_3]_0$ = 0.015 M.

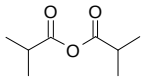
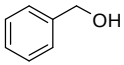
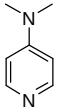
Results:

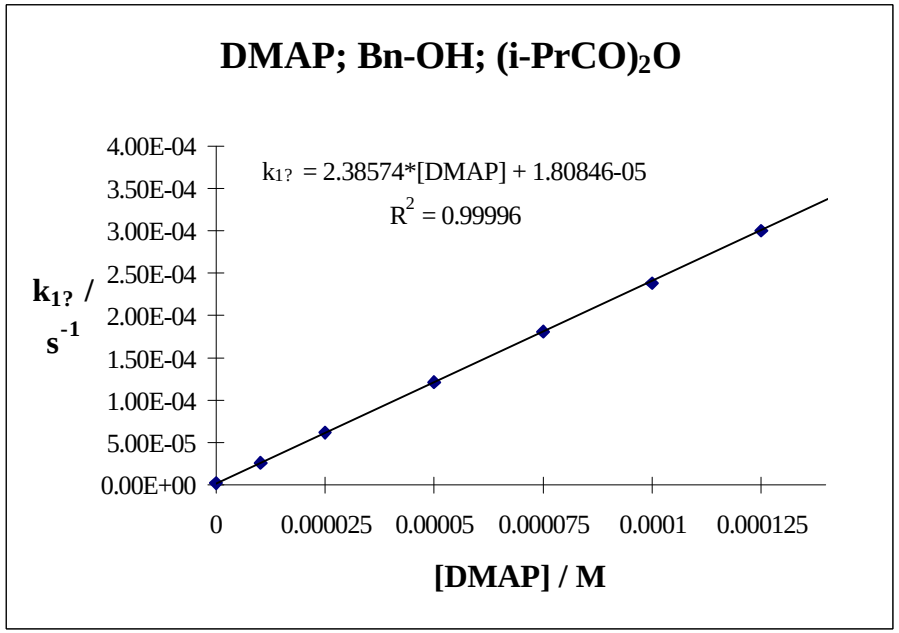
$k_2*[(RCO)_2O]_0 = 5.320 \pm 0.176 \times 10^{-5}\ s^{-1}$ => $k_2 = 1.773 \pm 0.059 \times 10^{-3}\ M^{-1}\ s^{-1}$

$k_3*[(RCO)_2O]_0 = 1.215 \pm 0.008 \times 10^{0}\ M^{-1}\ s^{-1}$ => $k_3 = 4.049 \pm 0.028\ 10^{+1}\ M^{-2}\ s^{-1}$

catalytic efficiency: $k_3*0.001/k_2$ = **22.835**

Supplemental Table 9: Rate Data for the transfer reaction of iso-butyric anhydride and Bn-OH in CH_2Cl_2 at 20 °C in the presence of DMAP as catalyst and triethylamine as auxiliary base (component ratio: alcohol/amine/anhydride = 1:3:6).

 / M	 / M	 / M	 / M	conversion / %	$k_{1?}$ / s^{-1}
0.12	0.02	0.06	0.0	35.5	1.670E-06
0.12	0.02	0.06	0.00001	84.1	2.510E-05
0.12	0.02	0.06	0.000025	84.1	6.293E-05
0.12	0.02	0.06	0.00005	83.8	1.207E-04
0.12	0.02	0.06	0.000075	80.4	1.809E-04
0.12	0.02	0.06	0.0001	80.7	2.389E-04
0.12	0.02	0.06	0.000125	85.0	3.011E-04



Supplemental Figure 9: Dependence of $k_{1\Psi}$ on the varying concentration of DMAP with $[(i\text{-}PrCO)_2O]_0$ = 0.12 M, $[Bn\text{-}OH]_0$ = 0.02 M, $[NEt_3]_0$ = 0.06 M.

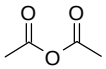
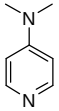
Results:

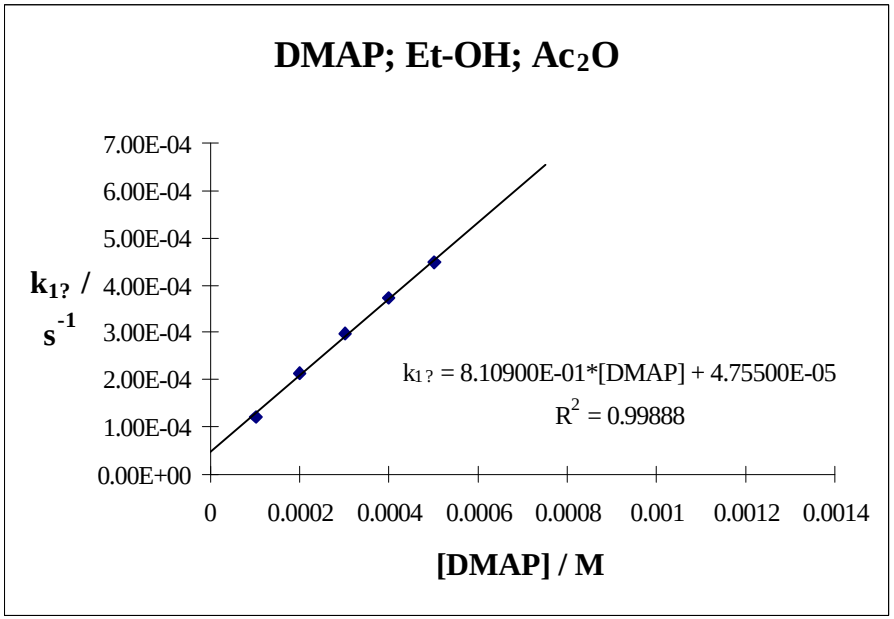
$k_2*[(RCO)_2O]_0 = 1.808 \pm 0.487 \times 10^{-6}\ s^{-1}$ => $k_2 = 1.507 \pm 0.406 \times 10^{-5}\ M^{-1}\ s^{-1}$

$k_3*[(RCO)_2O]_0 = 2.386 \pm 0.008 \times 10^{0}\ M^{-1}\ s^{-1}$ => $k_3 = 1.988 \pm 0.006\ 10^{+1}\ M^{-2}\ s^{-1}$

catalytic efficiency: $k_3*0.001/k_2$ = **1319.21**

Supplemental Table 10: Rate Data for the transfer reaction of acetic anhydride and Et-OH in CH_2Cl_2 at 20 °C in the presence of DMAP as catalyst and triethylamine as auxiliary base (component ratio: alcohol/amine/anhydride = 1:3:6).

 / M	 / M	 / M	 / M	conversion / %	$k_{1?}$ / s^{-1}
0.06	0.01	0.03	0.0001	58.2	1.221E-04
0.06	0.01	0.03	0.0002	68.9	2.128E-04
0.06	0.01	0.03	0.0003	72.7	2.985E-04
0.06	0.01	0.03	0.0004	74.5	3.735E-04
0.06	0.01	0.03	0.0005	80.5	4.472E-04



Supplemental Figure 10: Dependence of $k_{1\Psi}$ on the varying concentration of DMAP with [$(Ac_2O]_0$ = 0.06 M, [Et-OH]$_0$ = 0.01 M, [$NEt_3]_0$ = 0.03 M.

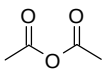
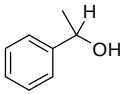
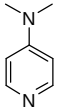
Results:

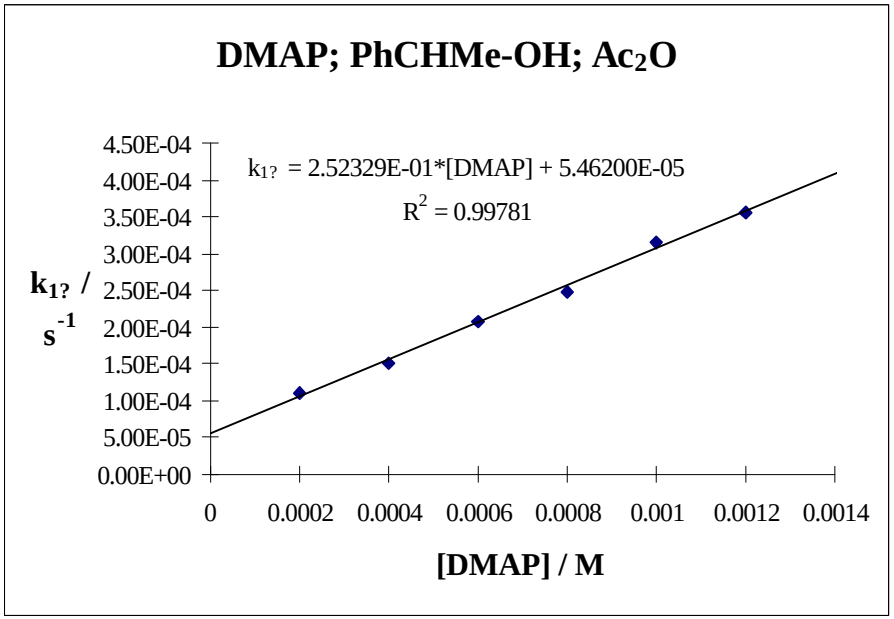
$k_2*[(RCO)_2O]_0 = 4.755 \pm 0.271 \times 10^{-5}\ s^{-1}$ => $k_2 = 7.925 \pm 0.452 \times 10^{-4}\ M^{-1}\ s^{-1}$

$k_3*[(RCO)_2O]_0 = 8.109 \pm 0.082 \times 10^{-1}\ M^{-1}\ s^{-1}$ => $k_3 = 1.352 \pm 0.014\ 10^{+1}\ M^{-2}\ s^{-1}$

catalytic efficiency: $k_3*0.001/k_2$ = **17.054**

Supplemental Table 11: Rate Data for the transfer reaction of acetic anhydride and PhCHMe-OH in CH_2Cl_2 at 20 °C in the presence of DMAP as catalyst and triethylamine as auxiliary base (component ratio: alcohol/amine/anhydride = 1:3:6).

 / M	 / M	 / M	 / M	conversion / %	$k_{1?}$ / s^{-1}
0.09	0.015	0.045	0.0002	66.7	1.092E-04
0.09	0.015	0.045	0.0004	72.1	1.514E-04
0.09	0.015	0.045	0.0006	72.7	2.072E-04
0.09	0.015	0.045	0.0008	73.2	2.481E-04
0.09	0.015	0.045	0.001	76.6	3.162E-04
0.09	0.015	0.045	0.0012	78.6	3.554E-04



Supplemental Figure 11: Dependence of $k_{1\Psi}$ on the varying concentration of DMAP with $[(Ac_2O]_0$ = 0.09 M, $[PhCHMe\text{-}OH]_0$ = 0.015 M, $[NEt_3]_0$ = 0.045 M.

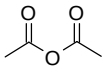
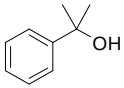
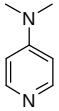
Results:

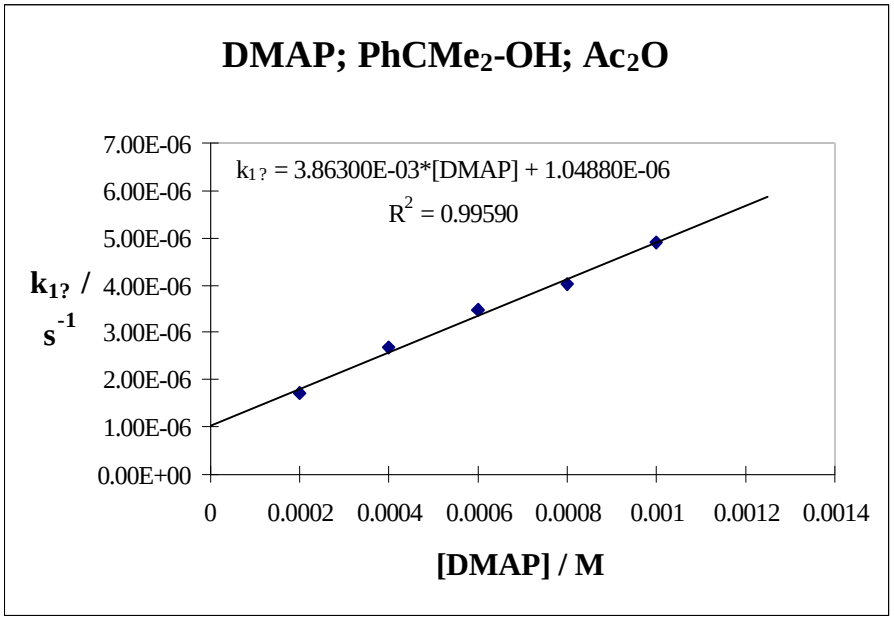
$k_2*[(RCO)_2O]_0 = 5.462 \pm 0.255 \times 10^{-5}\ s^{-1}$ => $k_2 = 6.069 \pm 0.283 \times 10^{-4}\ M^{-1}\ s^{-1}$

$k_3*[(RCO)_2O]_0 = 2.523 \pm 0.033 \times 10^{-1}\ M^{-1}\ s^{-1}$ => $k_3 = 2.804 \pm 0.036\ 10^{0}\ M^{-2}\ s^{-1}$

catalytic efficiency: $k_3*0.001/k_2$ = **4.620**

Supplemental Table 12: Rate Data for the transfer reaction of acetic anhydride and $PhCMe_2$-OH in CH_2Cl_2 at 20 °C in the presence of DMAP as catalyst and triethylamine as auxiliary base (component ratio: alcohol/amine/anhydride = 1:3:6).

 / M	 / M	 / M	 / M	conversion / %	$k_{1?}$ / s^{-1}
0.12	0.02	0.06	0.0002	50.2	1.712E-06
0.12	0.02	0.06	0.0004	49.5	2.690E-06
0.12	0.02	0.06	0.0006	59.1	3.495E-06
0.12	0.02	0.06	0.0008	55.0	4.032E-06
0.12	0.02	0.06	0.001	64.8	4.904E-06



Supplemental Figure 12: Dependence of $k_{1\Psi}$ on the varying concentration of DMAP with [$(Ac_2O]_0$ = 0.12 M, [$PhCMe_2$-$OH]_0$ = 0.02 M, [$NEt_3]_0$ = 0.06 M.

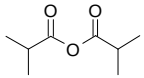
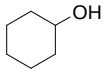
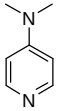
Results:

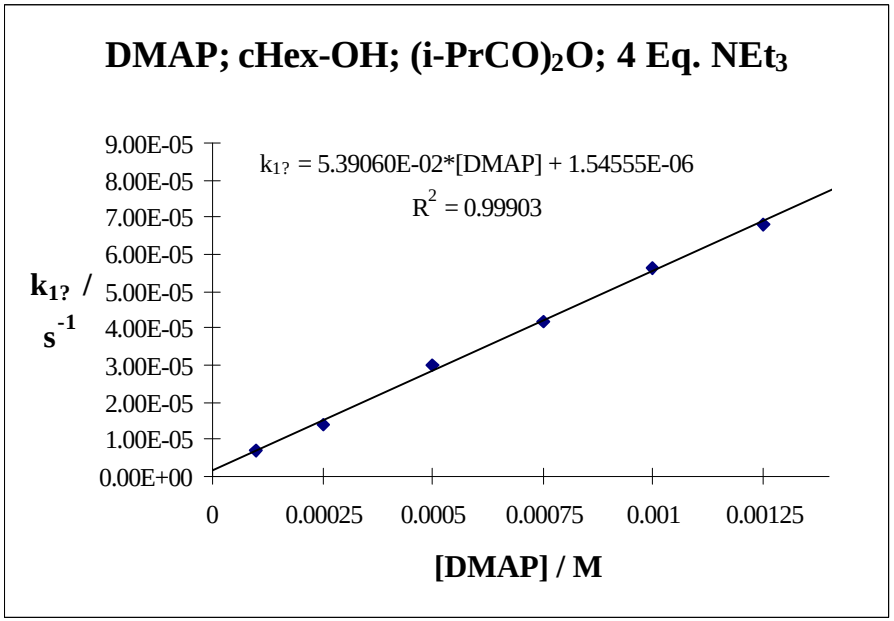
$k_2*[(RCO)_2O]_0 = 1.049 \pm 0.050 \times 10^{-6}\ s^{-1}$ => $k_2 = 8.740 \pm 0.413 \times 10^{-6}\ M^{-1}\ s^{-1}$

$k_3*[(RCO)_2O]_0 = 3.863 \pm 0.075 \times 10^{-3}\ M^{-1}\ s^{-1}$ => $k_3 = 3.219 \pm 0.062\ 10^{-2}\ M^{-2}\ s^{-1}$

catalytic efficiency: $k_3*0.001/k_2$ = **3.683**

Supplemental Table 13: Rate Data for the transfer reaction of iso-butyric anhydride and cyclohexanol in CH_2Cl_2 at 20 °C in the presence of DMAP as catalyst and triethylamine as auxiliary base (component ratio: alcohol/amine/anhydride = 1:4:6).

 / M	 / M	 / M	 / M	conversion / %	$k_{1?}$ / s^{-1}
0.12	0.02	0.08	0.0001	62.3	6.716E-06
0.12	0.02	0.08	0.00025	74.8	1.399E-05
0.12	0.02	0.08	0.0005	70.0	2.995E-05
0.12	0.02	0.08	0.00075	75.7	4.186E-05
0.12	0.02	0.08	0.001	73.1	5.647E-05
0.12	0.02	0.08	0.00125	77.0	6.782E-05



Supplemental Figure 13: Dependence of $k_{1\Psi}$ on the varying concentration of DMAP with $[(i\text{-}PrCO)_2O]_0$ = 0.12 M, $[cyclohexanol]_0$ = 0.02 M, $[NEt_3]_0$ = 0.08 M.

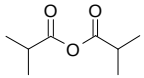
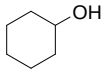
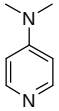
Results:

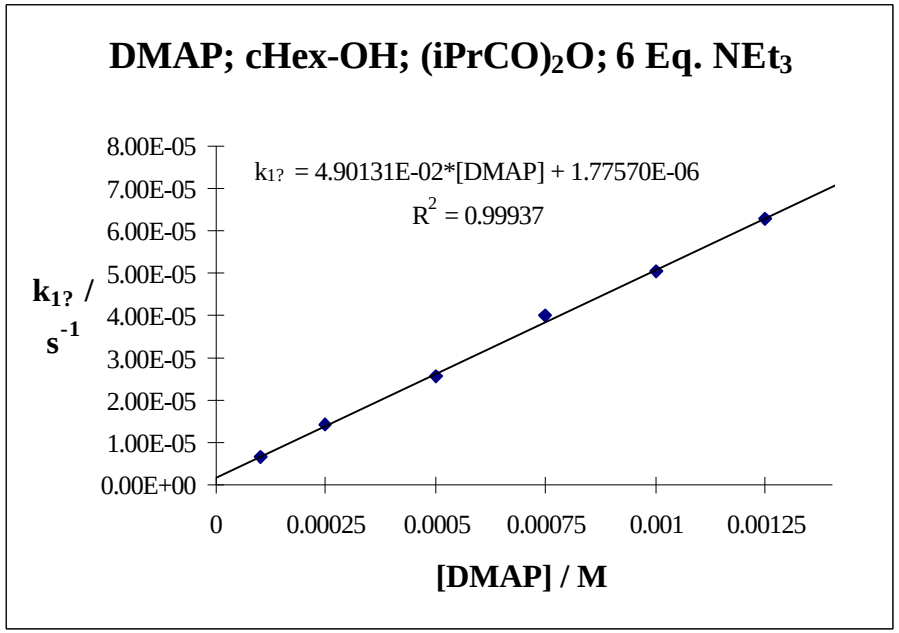
$k_2*[(RCO)_2O]_0 = 1.546 \pm 0.4289 \times 10^{-6}\ s^{-1}$ => $k_2 = 1.288 \pm 0.357 \times 10^{-5}\ M^{-1}\ s^{-1}$

$k_3*[(RCO)_2O]_0 = 5.391 \pm 0.057 \times 10^{-2}\ M^{-1}\ s^{-1}$ => $k_3 = 4.492 \pm 0.047\ 10^{-1}\ M^{-2}\ s^{-1}$

catalytic efficiency: $k_3*0.001/k_2$ = **34.878**

Supplemental Table 14: Rate Data for the transfer reaction of iso-butyric anhydride and cyclohexanol in CH_2Cl_2 at 20 °C in the presence of DMAP as catalyst and triethylamine as auxiliary base (component ratio: alcohol/amine/anhydride = 1:6:6).

 / M	 / M	 / M	 / M	conversion / %	$k_{1?}$ / s^{-1}
0.12	0.02	0.12	0.0001	72.4	6.597E-06
0.12	0.02	0.12	0.00025	77.5	1.408E-05
0.12	0.02	0.12	0.0005	66.7	2.553E-05
0.12	0.02	0.12	0.00075	74.8	3.999E-05
0.12	0.02	0.12	0.001	74.2	5.032E-05
0.12	0.02	0.12	0.00125	78.4	6.284E-05



Supplemental Figure 14: Dependence of $k_{1\Psi}$ on the varying concentration of DMAP with $[(i\text{-}PrCO)_2O]_0$ = 0.12 M, $[cyclohexanol]_0$ = 0.02 M, $[NEt_3]_0$ = 0.12 M.

Results:

$k_2*[(RCO)_2O]_0 = 1.776 \pm 0.313 \times 10^{-6}\ s^{-1}$ => $k_2 = 1.480 \pm 0.261 \times 10^{-5}\ M^{-1}\ s^{-1}$

$k_3*[(RCO)_2O]_0 = 4.901 \pm 0.041 \times 10^{-2}\ M^{-1}\ s^{-1}$ => $k_3 = 4.084 \pm 0.034\ 10^{-1}\ M^{-2}\ s^{-1}$

catalytic efficiency: $k_3*0.001/k_2$ = **27.602**

Literature

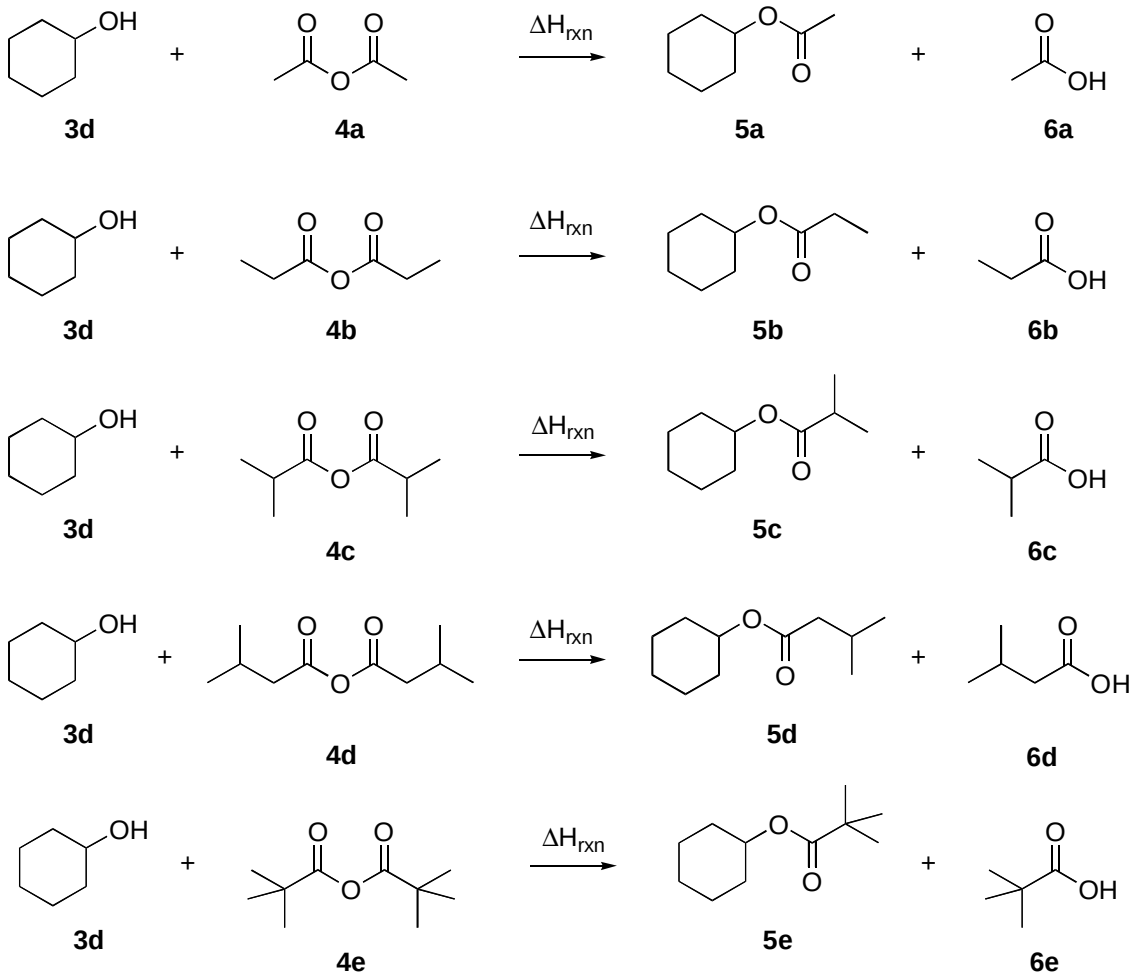
[1] Brindaban C. Ranu, Suvendu S. Dey, Alakananda Hajra, *Green Chemistry* **2003**, *5*, 44-46.

Computational Details

- Cyclohexanol + Various Anhydrides -

All stationary points have been optimized at the Becke3LYP/6-31G(d) level of theory. For all stationary points a number of conformational isomers exist. Only the energetically most favorable conformer has been used to generate the enthalpy profile discussed in the text. The nature of all stationary points has been verified through calculation of the vibrational frequency spectrum. Thermochemical corrections to calculate enthalpies at 298 K have been obtained using the rigid rotor/harmonic oscillator model and the force constants calculated at Becke3LYP/6-31G(d) level. Single point calculations have subsequently been performed at the Becke3LYP/6-311+G(d,p) level of theory. Combination of the single point energies with thermochemical corrections calculated at Becke3LYP/6-31G(d) level yields the "H_{298}" values cited in the text. Based on the Becke3LYP/6-31G(d) structures relative enthalpies at 298.15 K have

also been determined used the G3(MP2)B3 compound method. All calculations have been performed using Gaussian 03, Rev. B.03.


OH
O
O
O
ΔHrxn
O
O
O
OH
3d
4a
5a
6a
3d
4b
5b
6b
3d
4c
5c
6c
3d
4d
5d
6d
3d
4e
5e
6e

Scheme 1

Supplemental Table 1a. Energies for Reactants and Products in the Uncatalyzed Reaction of Acetic Anhydride (**4a**) + Cyclohexanol (**3d**) as Optimized at the Becke3LYP/6-31G(d) Level of Theory. Total Energies are in Hartree, Relative Enthalpies in kJ/mol.

reactants and products

stationary point	Etot (B3LYP/6-31G(d))	H298 (B3LYP/6-31G(d))	Etot (B3LYP/6-311+G(d,p)//B3LYP/6-31G(d))	"H298" (B3LYP/6-311+G(d,p)//B3LYP/6-31G(d))	"ΔH298" (B3LYP/6-311+G(d,p)//B3LYP/6-31G(d))
acetic anhydride (**4a**)	-381.727898	-381.620018	-381.847722	-381.739842	-
cyclohexanol (**3d**) upy40	-311.0902304	-310.907077	-311.1885776	-311.0054242	-
cyclohexanol (**3d**) upy41	-311.0903417	-310.907211	-311.1883248	-311.0051941	-
cyclohexyl acetate (**5a**) upy42	-463.7625208	-463.537634	-463.8964326	-463.6715458	-
cyclohexyl acetate (**13**) upy42b	-463.7616591	-463.536688	-463.8952034	-463.6702323	-
cyclohexyl acetate (**5a**) upy43	-463.7583472	-463.533411	-463.8916388	-463.6667026	-
acetic acid (**6a**) cpy3dx	-229.081787	-229.014236	-229.164574	-229.097023	-
3d + **4a**					0.0
5a + **6a**					-61.2

Supplemental Table 1b. Energies for Reactants and Products in the Uncatalyzed Reaction of Acetic Anhydride (**4a**) + Cyclohexanol (**3d**) at the G3MP2B3 Level of Theory. Total Energies are in Hartree, Relative Enthalpies in kJ/mol.

reactants and products

stationary point	DH298 (B3LYP/6-31G(d))	Etot (MP2(FC)/6-31G(d)// B3LYP/6-31G(d))	Etot (MP2(FC)/G3MP2large// B3LYP/6-31G(d))	Etot (QCISD(T)//6-31G(d)// B3LYP/6-31G(d))	HLC	H298 (G3MP2B3)
acetic anhydride (**4a**) cpy2cx	+0.104109	-380.6179376	-381.0451949	-380.6911444	-0.200820	-381.215113
cyclohexanol (**3d**) upy40	+0.176392	-310.0216809	-310.4209565	-310.1233781	-0.210861	-310.557123
cyclohexanol (**3d**) upy41	+0.176372	-310.0215052	-310.4205496	-310.1233233	-0.210861	-310.556857
cyclohexyl acetate (**5a**) upy42	+0.216667	-462.2482698	-462.8027063	-462.3807590	-0.291189	-463.009718
cyclohexyl acetate (**5a**) upy42b	+0.216745	-462.2486674	-462.8024055	-462.3809972	-0.291189	-463.009179
acetic acid (**6a**) cpy3dxsp6	+0.065161	-228.4187541	-228.6891450	-228.4608429	-0.120492	-228.786565
3d + **4a**						0.0
5a + **6a**						-63.1

Supplemental Table 2a. Energies for Reactants and Products in the Reaction of Propionic Anhydride (**4b**) + Cyclohexanol (**3d**) as Optimized at the Becke3LYP/6-31G(d) Level of Theory. Total Energies are in Hartree, Relative Enthalpies in kJ/mol.

reactants and products

stationary point	Etot (B3LYP/6-31G(d))	H298 (B3LYP/6-31G(d))	Etot (B3LYP/6-311+G(d,p)// B3LYP/6-31G(d))	"H298" (B3LYP/6-311+G(d,p)// B3LYP/6-31G(d))	"ΔH298" (B3LYP/6-311+G(d,p)// B3LYP/6-31G(d))
propionic anhydride (**4b**) upy45_01	-460.3579638	-460.189986	-460.4978364	-460.3298586	-
propionic anhydride (**4b**) upy45_02	-460.3573897	-460.189268	-460.4965542	-460.3284325	-
propionic anhydride (**4b**) upy45_03	-460.3563409	-460.188076	-460.4964024	-460.3281375	-
propionic anhydride (**4b**) upy45_04	-460.3559163	-460.187558	-460.4952385	-460.3268802	-
propionic anhydride (**4b**) upy45_07	-460.3555705	-460.187192	-460.4950115	-460.3266330	-
propionic anhydride (**4b**) upy45_06	-460.3546710	-460.186177	-460.4949244	-460.3264304	-
propionic anhydride (**4b**) upy45_05	-460.3543765	-460.185877	-460.4944804	-460.3255619	-
propionic anhydride (**4b**) upy45_08	-460.3540549	-460.185458	-460.4935794	-460.3249825	-
cyclohexanol (**3d**) upy40	-311.0902304	-310.907077	-311.1885776	-311.0054242	-

cyclohexanol (**3d**) upy41	-311.0903417	-310.907211	-311.1883248	-311.0051941	-
cyclohexyl propionate (**5b**) upy44_01	-503.0772186	-502.822278	-503.2209911	-502.9660505	-
cyclohexyl propionate (**5b**) upy44_02	-503.0763689	-502.821375	-503.2197596	-502.9647657	-
cyclohexyl propionate (**5b**) upy44_03	-503.0757777	-502.820544	-503.2196517	-502.9644180	-
cyclohexyl propionate (**5b**) upy44_04	-503.0757442	-502.820524	-503.2196356	-502.9644154	-
cyclohexyl propionate (**5b**) upy44_07	-503.0748971	-502.819621	-503.2184475	-502.9631714	-
cyclohexyl propionate (**5b**) upy44_06	-503.0747795	-502.819553	-503.2182850	-502.9630585	-
cyclohexyl propionate (**5b**) upy44_05	-503.0730532	-502.818957	-503.2162042	-502.9621080	-
propionic acid (**6b**) upy46b	-268.3966257	-268.299028	-268.4893189	-268.3917212	-
propionic acid (**6b**) upy46a	-268.3949673	-268.297126	-268.4879116	-268.3900703	
3d + **4b**					0.0
5b + **6b**					-59.0

Supplemental Table 2b. Energies for Reactants and Products in the Reaction of Propionic Anhydride (**4b**) + Cyclohexanol (**3d**) at the QCISD(T) Level of Theory. Total Energies are in Hartree, Relative Enthalpies in kJ/mol.

reactants and products

stationary point	DH298 (B3LYP/6-31G(d))	Etot (MP2(FC)/6-31G(d)// B3LYP/6-31G(d))	Etot (MP2(FC)/G3MP2large// B3LYP/6-31G(d))	Etot (QCISD(T)/6-31G(d)// B3LYP/6-31G(d))	HLC	Etot (G3MP2B3)
propionic anhydride (**4b**) upy45_01	+0.161989	-458.9514043	-459.4816229	-459.0572041	-0.261066	-459.6864997
propionic anhydride (**4b**) upy45_02	+0.162126	-458.9498720	-459.4805116	-459.0560122	-0.261066	-459.6855918
propionic anhydride (**4b**) upy45_03	+0.162261	-458.9502161	-459.4805020	-459.0558873	-0.261066	-459.6849782
cyclohexanol (**3d**) upy40	+0.176392	-310.0216809	-310.4209565	-310.1233781	-0.210861	-310.557123
cyclohexanol (**3d**) upy41	+0.176372	-310.0215052	-310.4205496	-310.1233233	-0.210861	-310.556857
cyclohexyl propionate (**5b**) upy44_01	+0.245611	-501.4147819	-502.0205421	-501.5635764	-0.321312	-502.2450376
cyclohexyl propionate (**5b**) upy44_02	+0.245661	-501.4152327	-502.0203177	-501.5638577	-0.321312	-502.2445937
cyclohexyl propionate (**5b**) upy44_03	+0.245889	-501.4137766	-502.0194861	-501.562438	-0.321312	-502.2435705
propionic acid (**6b**) upy46b	+0.094099	-267.5851382	-267.9069725	-267.643512	-0.150615	-268.0218623
propionic acid (**6b**) upy46a	+0.094330	-267.5836744	-267.9055139	-267.641980	-0.150615	-268.0201045
3d + **4b**						0.0
5b + **6b**						-61.1

Supplemental Table 3a. Energies for all Stationary Points Located on the Potential Energy Surface of Isobutyric Anhydride (**4c**) + Cyclohexanol (**3d**) as Optimized at the Becke3LYP/6-31G(d) Level of Theory. Total Energies are in Hartree, Relative Enthalpies in kJ/mol.

reactants and products

stationary point	Etot (B3LYP/6-31G(d))	H298 (B3LYP/6-31G(d))	Etot (B3LYP/6-311+G(d,p)// B3LYP/6-31G(d))	"H298" (B3LYP/6-311+G(d,p)// B3LYP/6-31G(d))	"ΔH298" (B3LYP/6-311+G(d,p)// B3LYP/6-31G(d))
isobutyric anhydride (**4a**) upy26	-538.9853911	-538.757818	-539.1457937	-538.9182206	-
isobutyric anhydride (**4c**) upy25	-538.985017610	-538.757445	-539.145246394	-538.9176738	-
isobutyric anhydride (**4c**) upy27	-538.984625187	-538.757042	-539.144696010	-538.9171128	-
isobutyric anhydride (**4c**) upy28	-538.984143991	-538.756455	-539.144391865	-538.9167029	-
isobutyric anhydride (**4c**) upy30	-538.983940717	-538.756219	-539.144177257	-538.9164555	-
isobutyric anhydride (**4c**) upy29	-538.984042434	-538.756146	-539.143768956	-538.9158726	-
cyclohexanol (**3d**) upy40	-311.0902304	-310.907077	-311.1885776	-311.0054242	-
cyclohexanol (**3d**) upy41	-311.0903417	-310.907211	-311.1883248	-311.0051941	-
cyclohexyl isobutyrate (**5c**) upy47_01	-542.3909012	-542.106203	-542.5447796	-542.260081	-
cyclohexyl isobutyrate	-542.3909015	-542.106136	-542.5448061	-542.260040	-

(**5c**) upy47_02					
cyclohexyl isobutyrate (**5c**) upy47_03	-542.3899611	-542.105113	-542.54397	-542.259122	-
cyclohexyl isobutyrate (**5c**) upy47_04	-542.3867307	-542.101816	-542.5400582	-542.255144	-
cyclohexyl isobutyrate (**5c**) upy47_05	-542.3857998	-542.100892	-542.5392262	-542.254318	-
cyclohexyl isobutyrate (**5c**) upy47_06	-542.3765459	-542.091929	-542.5308631	-542.246246	-
isobutyric acid (**6c**) upy32	-307.7102188	-307.582823	-307.8131518	-307.685756	-
isobutyric acid (**6c**) upy31 (ts)	-307.7097888	-307.583197	-307.8127944	-307.686203	-
isobutyric acid (**6c**) upy35	-307.7091445	-307.581700	-307.8123613	-307.684917	-
3d + **4c**					0.0
5c + **6c**					-58.3

Supplemental Table 3b. Energies for all Stationary Points Located on the Potential Energy Surface of Isobutyric Anhydride (**4c**) + Cyclohexanol (**3d**) at the G3MP2B3 Level of Theory. Total Energies are in Hartree, Relative Enthalpies in kJ/mol.

reactants and products

stationary point	D298 (B3LYP/6-31G(d))	Etot (MP2(FC)/6-31G(d)// B3LYP/6-31G(d))	Etot (MP2(FC)/G3MP2large/ / B3LYP/6-31G(d))	Etot (QCISD(T)//6-31G(d)// B3LYP/6-31G(d))	HLC	H298 (G3MP2B3)
isobutyric anhydride (**4c**) upy26	+0.219409	-537.2873793	-537.9216151	-537.4247717	-0.321312	-538.1609105
isobutyric anhydride (**4c**) upy25	+0.219407	-537.2869774	-537.9210013	-537.4244059	-0.321312	-538.1603348
isobutyric anhydride (**4c**) upy27	+0.219418	-537.2865151	-537.9203102	-537.4239840	-0.321312	-538.1596731
cyclohexanol (**3d**) upy40	+0.176392	-310.0216809	-310.4209565	-310.1233781	-0.210861	-310.557123
cyclohexanol (**3d**) upy41	+0.176372	-310.0215052	-310.4205496	-310.1233233	-0.210861	-310.556857
cyclohexyl isobutyrate (**5c**) upy47_01	+0.274284	-540.5828365	-541.2404345	-540.7474106	-0.351435	-541.4821596
cyclohexyl isobutyrate (**5c**) upy47_02	+0.274346	-540.5827578	-541.2403173	-540.7473499	-0.351435	-541.4819984
cyclohexyl isobutyrate (**5c**) upy47_03	+0.274425	-540.5822315	-541.2397726	-540.7466931	-0.351435	-541.4812442
isobutyric acid (**6c**) upy32	+0.122808	-306.7525404	-307.1262593	-306.8267685	-0.180738	-307.2584174
3d + **4c**						0.0

5c + 6c						-59.2

Supplemental Table 4a. Energies for all Stationary Points Located on the Potential Energy Surface of 3-Methylbutyric Anhydride (**4d**) + Cyclohexanol (**3d**) as Optimized at the Becke3LYP/6-31G(d) Level of Theory. Total Energies are in Hartree, Relative Enthalpies in kJ/mol.

reactants and products

stationary point	Etot (B3LYP/6-31G(d))	H298 (B3LYP/6-31G(d))	Etot (B3LYP/6-311+G(d,p)// B3LYP/6-31G(d))	"H298" (B3LYP/6-311+G(d,p)// B3LYP/6-31G(d))	"ΔH298" (B3LYP/6-311+G(d,p)// B3LYP/6-31G(d))
3-methylbutyric anhydride (**4d**) upy49_02	-617.6136024	-617.326650	-617.7954059	-617.508454	-
3-methylbutyric anhydride (**4d**) upy49_01	-617.6134397	-617.326540	-617.7951410	-617.508241	-
3-methylbutyric anhydride (**4d**) upy49_05	-617.6131472	-617.325983	-617.7946844	-617.507520	-
3-methylbutyric anhydride (**4d**) upy49_06	-617.6129479	-617.325850	-617.7944294	-617.507332	-
3-methylbutyric anhydride (**4d**) upy49_04	-617.6128580	-617.325855	-617.7940558	-617.507053	-
3-methylbutyric anhydride (**4d**) upy49_03	-617.6128741	-617.325869	-617.7939991	-617.506994	-
3-methylbutyric anhydride (**4d**) upy49_08	-617.6129004	-617.325466	-617.7938634	-617.506429	-
3-methylbutyric anhydride (**4d**) upy49_10	-617.6121385	-617.324821	-617.7935950	-617.506278	-
3-methylbutyric anhydride (**4d**) upy49_09	-617.6119470	-617.324713	-617.7933385	-617.506105	-

3-methylbutyric anhydride (**4d**) upy49_07	-617.6118084	-617.324821	-617.7930454	-617.506058	-
cyclohexanol (**3d**) upy40	-311.0902304	-310.907077	-311.1885776	-311.0054242	-
cyclohexanol (**3d**) upy41	-311.0903417	-310.907211	-311.1883248	-311.0051941	-
cyclohexyl 3-methylbutyrate (**5d**) upy50_02	-581.7051778	-581.390700	-581.8698385	-581.5553607	-
cyclohexyl 3-methylbutyrate (**5d**) upy50_01	-581.7051336	-581.390682	-581.8697602	-581.5553086	-
cyclohexyl 3-methylbutyrate (**5d**) upy50_06	-581.7041263	-581.389504	-581.8690001	-581.5543778	-
cyclohexyl 3-methylbutyrate (**5d**) upy50_05	-581.7040912	-581.389418	-581.8688998	-581.5542266	-
cyclohexyl 3-methylbutyrate (**5d**) upy50_04	-581.7042932	-581.389748	-581.868570	-581.5540245	-
cyclohexyl 3-methylbutyrate (**5d**) upy50_08	-581.7030354	-581.388378	-581.8673957	-581.5527383	-
cyclohexyl 3-methylbutyrate (**5d**) upy50_10	-581.7008996	-581.386445	-581.8649399	-581.5504853	-
cyclohexyl 3-methylbutyrate (**5d**) upy50_03	-581.7042416	-581.389808	-581.8685026	-581.554069	-
cyclohexyl 3-methylbutyrate (**5d**) upy50_09	-581.7032797	-581.388472	-581.8677289	-581.552921	-
cyclohexyl 3-methylbutyrate (**5d**) upy50_07	-581.7033978	-581.388830	-581.8674548	-581.552887	-
3-methylbutyric acid (**6d**) upy69_01	-347.0245177	-346.867437	-347.1380636	-346.980983	-

3-methylbutyric acid (**6d**) upy69_02	-347.0233146	-346.866052	-347.1373209	-346.980058	-
3-methylbutyric acid (**6d**) upy69_03	-347.0229478	-346.865752	-347.1359967	-346.978801	-
3-methylbutyric acid (**6d**) upy69_04	-347.0222719	-346.864822	-347.1355496	-346.978100	-
3-methylbutyric acid (**6d**) upy69_05	-347.0152622	-346.858451	-347.1293415	-346.972530	
3d + **4d**					0.0
5d + **6d**					-59.0

Supplemental Table 4b. Energies for Reactants and Products in the Uncatalyzed Reaction of 3-Methylbutyric Anhydride (**4d**) + Cyclohexanol (**3d**) at the G3MP2B3 Level of Theory. Total Energies are in Hartree, Relative Enthalpies in kJ/mol.

reactants and products

stationary point	DH298 (B3LYP/6-31G(d))	Etot (MP2(FC)/6-31G(d)// B3LYP/6-31G(d))	Etot (MP2(FC)/G3MP2large/ / B3LYP/6-31G(d))	Etot (QCISD(T)//6-31G(d)// B3LYP/6-31G(d))	HLC	H298 (G3MP2B3)
3-methylbutyric anhydride (**4d**) upy49_05	+0.276800	-615.6205150	-616.3585243	-615.7902798	-0.381558	-616.633047
3-methylbutyric anhydride (**4d**) upy49_06	+0.276737	-615.6202641	-616.3581886	-615.7900676	-0.381558	-616.632813
3-methylbutyric anhydride (**4d**) upy49_02	+0.276599	-615.6195471	-616.3576817	-615.7895759	-0.381558	-616.632670
3-methylbutyric anhydride (**4d**) upy49_01	+0.276549	-615.6193671	-616.3574186	-615.7894337	-0.381558	-616.632494
3-methylbutyric anhydride (**4d**) upy49_04	+0.276647	-615.6182489	-616.3568606	-615.7886123	-0.381558	-616.632135
cyclohexanol (**3d**) upy40	+0.176392	-310.0216809	-310.4209565	-310.1233781	-0.210861	-310.557123
cyclohexanol (**3d**) upy41	+0.176372	-310.0215052	-310.4205496	-310.1233233	-0.210861	-310.556857
cyclohexyl 3-methylbutyrate (**5d**) upy50_01	+0.302938	-579.7491169	-580.4587839	-579.9299915	-0.381558	-580.718279
cyclohexyl 3-methylbutyrate (**5d**) upy50_02	+0.302963	-579.7490732	-580.4587188	-579.9299462	-0.381558	-580.718187

cyclohexyl 3-methylbutyrate (**5d**) upy50_05	+0.303149	-579.7490108	-580.4588027	-579.9296455	-0.381558	-580.717846
cyclohexyl 3-methylbutyrate (**5d**) upy50_04	+0.303025	-579.7495539	-580.4585286	-579.9302489	-0.381558	-580.717757
cyclohexyl 3-methylbutyrate (**5d**) upy50_06	+0.303101	-579.7489001	-580.4586724	-579.9295265	-0.381558	-580.717756
3-methylbutyric acid (**6d**) upy69_01	+0.151399	-345.9191588	-346.3448474	-346.0096347	-0.210861	-346.494785
3-methylbutyric acid (**6d**) upy69_02	+0.151573	-345.9184677	-346.3443643	-346.0087523	-0.210861	-346.493937
3-methylbutyric acid (**6d**) upy69_03	+0.151509	-345.9179425	-346.3429626	-346.0084687	-0.210861	-346.492841
3-methylbutyric acid (**6d**) upy69_04	+0.151749	-345.9177104	-346.3430977	-346.0079493	-0.210861	-346.492449
3d + **4d**						0.0
5d + **6d**						-60.1

Supplemental Table 5a. Energies for all Stationary Points Located on the Potential Energy Surface of Pivalic Anhydride (**4e**) + Cyclohexanol (**3d**) as Optimized at the Becke3LYP/6-31G(d) Level of Theory. Total Energies are in Hartree, Relative Enthalpies in kJ/mol.

reactants and products

stationary point	Etot (B3LYP/6-31G(d))	H298 (B3LYP/6-31G(d))	Etot (B3LYP/6-311+G(d,p)// B3LYP/6-31G(d))	"H298" (B3LYP/6-311+G(d,p)// B3LYP/6-31G(d))	"ΔH298" (B3LYP/6-311+G(d,p)// B3LYP/6-31G(d))
pivalic anhydride (**4e**) upy24	-617.6116891	-617.325592	-617.7921760	-617.5060789	-
cyclohexanol (**3d**) upy40	-311.0902304	-310.907077	-311.1885776	-311.0054242	-
cyclohexanol (**3d**) upy41	-311.0903417	-310.907211	-311.1883248	-311.0051941	-
cyclohexyl pivalate (**5e**) upy48_01	-581.7042329	-581.390269	-581.8680548	-581.5540909	-
cyclohexyl pivalate (**5e**) upy48_02	-581.6999587	-581.385890	-581.8632271	-581.5491584	-
cyclohexyl pivalate (**5e**) upy48_04	-581.6940089	-581.379950	-581.8580717	-581.5440128	-
cyclohexyl pivalate (**5e**) upy48_03	-581.6936375	-581.379529	-581.8576974	-581.5435889	-
cyclohexyl pivalate (**5e**) upy48_06	-581.6938167	-581.379774	-581.8580323	-581.5439896	-
cyclohexyl pivalate (**5e**) upy48_05	-581.6936887	-581.379515	-581.8578206	-581.5436469	-
cyclohexyl pivalate (**5e**) upy48_07	-581.6937102	-581.379656	-581.8573848	-581.5433306	-
cyclohexyl pivalate (**5e**) upy48_08	-581.6934178	-581.379295	-581.8573613	-581.5432385	-
cyclohexyl pivalate (**5e**) upy48_09	-581.6893743	-581.375128	-581.853016	-581.5387697	-
pivalic acid (**6e**) upy21	-347.0235871	-346.866960	-347.1366776	-346.9800505	-
3d + **4e**					0.0
5e + **6e**					-59.4

Supplemental Table 5b. Energies for all Stationary Points Located on the Potential Energy Surface of Pivalic Anhydride (**4e**) + Cyclohexanol (**3d**) at the G3MP2B3 Level of Theory. Total Energies are in Hartree, Relative Enthalpies in kJ/mol.

reactants and products

stationary point	DH298 (B3LYP/6-31G(d))	Etot (MP2(FC)/6-31G(d)// B3LYP/6-31G(d))	Etot (MP2(FC)/G3MP2large/ / B3LYP/6-31G(d))	Etot (QCISD(T)//6-31G(d)// B3LYP/6-31G(d))	HLC	H298 (G3MP2B3)
pivalic anhydride (**4e**) upy24	+0.275818	-615.6272631	-616.3656072	-615.7955004	-0.381558	-616.6395845
cyclohexanol 3d) upy40	+0.176392	-310.0216809	-310.4209565	-310.1233781	-0.210861	-310.557123
cyclohexanol (**3d**) upy41	+0.176372	-310.0215052	-310.4205496	-310.1233233	-0.210861	-310.556857
cyclohexyl pivalate (**5e**) upy48_01	+0.302490	-579.7528635	-580.4623149	-579.9328570	-0.381558	-580.7213764
cyclohexyl pivalate (**5e**) upy48_02	+0.302592	-579.7487129	-580.4580417	-579.9287958	-0.381558	-580.7170906
cyclohexyl pivalate (**5e**) upy48_04	+0.302584	-579.7427233	-580.4524772	-579.9229362	-0.381558	-580.7116641
pivalic acid (**6e**) upy21	+0.150983	-345.9220992	-346.3479104	-346.0117967	-0.210861	-346.4974859
3d + **4e**						0.0
5e + **6e**						-58.2

Structures of all Stationary Points

3d-a

1\1\GINC-CICUM81\SP\RB3LYP\6-311+G(d,p)\C6H12O1\ZIPSE\03-Jan-2006\0\\#
P BECKE3LYP/6-311+G(D,P) INT=FINEGRID SCF=(DIRECT,TIGHT) GEOM=CHECK GU
ESS=READ\\upy40 b3lyp/6-311+G(d,p)//b3lyp/6-31G(d) sp cyclohexanol\\0,
1\C,0,-1.4896831656,-0.6571764484,-0.9646910897\C,0,-1.490644454,-0.66
71350821,0.5720915801\C,0,-0.0579857206,-0.6650913256,1.1305232852\C,0

,0.7612681263,0.5113549999,0.5833864581\C,0,0.7688030211,0.5099090413,
-0.9450046243\C,0,-0.6584181566,0.5121914661,-1.5157222729\H,0,-0.0766
677529,-0.6279225458,2.2298417825\H,0,-2.0260975218,0.2209926766,0.939
1901253\H,0,-2.0401436621,-1.5383201488,0.9498909456\H,0,-1.0686287642
,-1.6046960827,-1.3316095387\H,0,-2.5182205784,-0.6041841766,-1.343725

7572\H,0,0.296925266,1.4530829127,0.9293178868\H,0,1.3381928155,1.3750
550507,-1.3047126039\H,0,1.3071317827,-0.3874900805,-1.2805389365\H,0,
-1.1533286095,1.4601232246,-1.2573615784\H,0,-0.621969727,0.4711588436
,-2.6113827849\H,0,0.4568852925,-1.5951519123,0.8518797273\O,0,2.12276

35524,0.45856141,1.0106234122\H,0,2.1237751372,0.444545052,1.9
80723416
\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-
311.1885776\RMSD=4.297e-0
9\Dipole=-0.627775,-0.035755,0.3108417\PG=C01 [X(C6H12O1)]\\@

4a-a

1\1\GINC-TERMINUS\SP\RB3LYP\6-311+G(d,p)\C4H6O3\ZIPSE\03-Jul-2003\0\\#
P BECKE3LYP/6-311+G(D,P) SCF=TIGHT GEOM=CHECK GUESS=READ INT=FINEGRID\
\cpy2cxsp1 b3lyp/6-311+G(d,p)//b3lyp/6-31G(d) sp\\0,1\X\O,1,1.\X,2,1.,
1,90.\C,2,1.3964600599,1,119.46349655,3,-90.,0\C,2,1.3964600599,1,119.
46349655,3,90.,0\O,4,1.1982668208,2,123.4803858,1,207.70069103,0\O,5,1
.1982668208,2,123.4803858,1,207.70069103,0\C,4,1.5065014938,6,126.8733
0163,2,182.93620837,0\C,5,1.5065014938,7,126.87330163,2,182.93620837,0
\H,8,1.0904887667,4,109.48533983,6,4.47766345,0\H,9,1.0904887667,5,109
.48533983,7,4.47766345,0\H,8,1.0957217967,4,109.58255241,10,-120.47036
079,0\H,8,1.0945955034,4,110.35036728,10,121.53064502,0\H,9,1.09572179
67,5,109.58255241,11,-120.47036079,0\H,9,1.0945955034,5,110.35036728,1
1,121.53064502,0\\Version=x86-Linux-G98RevA.7\State=1-A\HF=-381.847721
9\RMSD=3.138e-09\Dipole=0.,0.,-1.6249639\PG=C02 [C2(O1),X(C4H6O2)]\\@

4b-a

1\1\GINC-HAENSEL\SP\RB3LYP\6-311+G(d,p)\C6H10O3\ZIPSE\05-Jan-2006\0\\#
P BECKE3LYP/6-311+G(D,P) INT=FINEGRID SCF=(DIRECT,TIGHT) GEOM=CHECK GU
ESS=READ\\upy45_01 b3lyp/6-311+G(d,p)//b3lyp/6-31G(d) sp\\0,1\C,0,-1.6
096298888,0.2551787912,-3.3441178275\C,0,-1.651428102,-0.101406838,-1.
8596476371\C,0,-0.3666498943,0.2378576876,-1.138846827\O,0,-0.52820865
62,0.0403616097,0.233550371\C,0,0.5642930092,-0.2529377903,1.051455564
9\C,0,0.2838845814,0.2058840195,2.4643098981\C,0,1.3590111981,-0.23608
7407,3.4549246891\O,0,0.6421359769,0.6622700828,-1.6292253069\O,0,1.54
19513347,-0.8290906979,0.6635305946\H,0,-1.8324277553,-1.1746473693,-1
.7094335046\H,0,-2.4737080533,0.4076248395,-1.3409252254\H,0,-2.552060
1016,-0.0199382335,-3.8280283416\H,0,-1.4494910724,1.3282619632,-3.486
251783\H,0,-0.793896781,-0.2692415067,-3.8497898425\H,0,0.1895319481,1
.3001706597,2.4358820673\H,0,-0.7093735978,-0.1644011658,2.7483109461\
H,0,2.3402573496,0.1510612682,3.1661114474\H,0,1.1236404777,0.12895732
76,4.4596019654\H,0,1.4336129212,-1.3271065182,3.4932098384\\Version=x
86-Linux-G03RevB.03\State=1-A\HF=-460.4978364\RMSD=4.855e-09\Dipole=-1
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4c-a

1\1\GINC-MAX\SP\RB3LYP\6-311+G(d,p)\C8H14O3\ZIPSE\04-Dec-2005\0\\#P BE
CKE3LYP/6-311+G(D,P) SCF=TIGHT INT=FINEGRID GEOM=CHECK GUESS=READ\\upy
26 b3lyp/6-311+G(d,p)//b3lyp/6-31G(d) sp isobutyric anhydride\\0,1\C,0
,-1.1632640626,-0.4338175145,0.0855309991\O,0,-1.2719166069,-0.9732297
879,1.1516918782\O,0,0.0619759339,0.0101008264,-0.4191855292\C,0,-2.26
91812175,-0.1727505006,-0.9213784908\C,0,-3.5193913532,-0.9856320752,-
0.5745615434\C,0,-2.5571117104,1.3424634914,-0.9895077693\H,0,-3.30343
84429,-2.0581847325,-0.5470910498\H,0,-3.9070582796,-0.7012361548,0.40
85110194\H,0,-4.3017121353,-0.8100783189,-1.3205925262\H,0,-1.66160719
12,1.9085413681,-1.2619991827\H,0,-3.3297806328,1.5396984767,-1.740015
2451\H,0,-2.9194517906,1.7132286675,-0.0240849706\C,0,1.0857678664,0.4
211944264,0.4386414695\O,0,0.8776774695,0.9089991152,1.5148455043\C,0,
2.4374202244,0.2001648214,-0.2165357857\C,0,3.5282127933,0.9870561094,
0.5149399469\H,0,4.4940605339,0.8414111076,0.0196290689\H,0,3.30607976
27,2.058601691,0.5293086448\H,0,3.616977282,0.6539412188,1.553570679\C
,0,2.7432897752,-1.3121262608,-0.2698199171\H,0,3.7013501307,-1.479154
4241,-0.7732107177\H,0,2.813500818,-1.7305010569,0.7405420191\H,0,1.96
88276382,-1.8584698495,-0.8160258609\H,0,-1.8816638971,-0.4838557248,-
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083,0.0360907,-1.498225\PG=C01 [X(C8H14O3)]\\@

4d-a

1\1\GINC-HAENSEL\SP\RB3LYP\6-311+G(d,p)\C10H18O3\ZIPSE\07-Jan-2006\0\\
#P BECKE3LYP/6-311+G(D,P) INT=FINEGRID SCF=(DIRECT,TIGHT) GEOM=CHECK G
UESS=READ\\upy49_02 b3lyp/6-311+G(d,p)//b3lyp/6-31G(d) sp\\0,1\C,0,1.4
722438801,2.4379400933,-4.0434957525\C,0,1.7602252154,2.0532642567,-2.
585527671\C,0,3.1613440396,1.4414990262,-2.4396996441\C,0,0.6723185916
,1.1012630253,-2.0632088695\C,0,0.6992240765,0.8945920114,-0.565664940
5\O,0,-0.0544172119,-0.2311012966,-0.228499554\C,0,-0.6669466426,-0.33
59857298,1.0225018934\C,0,-0.7885677367,-1.7914524328,1.4126827063\C,0
,-1.7230724098,-2.049428157,2.6054694815\C,0,-3.1895828754,-1.77253959
62,2.2436722783\O,0,1.2866720359,1.5549909453,0.2461609997\O,0,-1.0502
075847,0.6166323154,1.6434010438\C,0,-1.5398224045,-3.4847486889,3.118
5469779\H,0,-1.1008236917,-2.3636380583,0.5292229651\H,0,0.2327260469,
-2.1336272348,1.6374009797\H,0,-1.4333355529,-1.3543644018,3.403905630
3\H,0,0.7279581515,0.1206965625,-2.553332242\H,0,-0.3293594147,1.49177
09573,-2.2978455701\H,0,1.7207988008,2.961777874,-1.9711229599\H,0,0.4
894955323,2.9131709586,-4.1490874437\H,0,2.2256811311,3.140726394,-4.4
167435874\H,0,1.4895433912,1.5562152203,-4.6974644332\H,0,3.9279722296

,2.1405314565,-2.7928223862\H,0,3.3846716276,1.2007227541,-1.3958701307\H,0,3.2514237656,0.5222809971,-3.033842318\H,0,-1.8017061919,-4.2187723235,2.3452135589\H,0,-0.503554298,-3.6754615877,3.4228466739\H,0,-2.1834677162,-3.6738505288,3.9850180139\H,0,-3.8403125345,-1.9388191357,3.1096913938\H,0,-3.3298116348,-0.738831225,1.9137901901\H,0,-3.5284599619,-2.441127241,1.4408829906\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-617.7954059\RMSD=4.304e-09\Dipole=-0.1190794,-0.9994281,-0.8825117\PG=C01 [X(C10H18O3)]\\@

4e-a

1\1\GINC-GRETEL\SP\RB3LYP\6-311+G(d,p)\C10H18O3\ZIPSE\05-Dec-2005\0\\# P BECKE3LYP/6-311+G(D,P) SCF=TIGHT INT=FINEGRID GEOM=CHECK GUESS=READ\ \upy24 b3lyp/6-311+G(d,p)//b3lyp/6-31G(d) sp pivalic anhydride\\0,1\C,0,-1.2085376412,-0.3863623412,0.4202368512\O,0,-1.3010348818,-0.8252200982,1.5334412378\O,0,0.0201727158,-0.0123240986,-0.1318040903\C,0,-2.3424342885,-0.2123451675,-0.5896818902\C,0,-2.0265057429,-1.0312266234,-1.8619236584\C,0,-3.6475664873,-0.7101875829,0.0509689373\C,0,-2.4572090044,1.2874844589,-0.9452813994\H,0,-1.1030543274,-0.6926251667,-2.3398467002\H,0,-1.9251669495,-2.0982320212,-1.632509454\H,0,-2.8461131215,-0.9191132502,-2.5808246862\H,0,-3.8816658484,-0.1485139049,0.960066265\H,0,-4.4762343736,-0.5893595585,-0.6555602733\H,0,-3.5771006698,-1.7674250449,0.3242548376\H,0,-3.2832619646,1.4344999963,-1.6502889275\H,0,-2.6617569426,1.8921170907,-0.0545941003\H,0,-1.5395718254,1.6601355683,-1.4095740736\C,0,1.0397679474,0.4895070819,0.6824304054\O,0,0.8100972844,1.1252493977,1.6741254813\C,0,2.41687859,0.1668495742,0.1032961162\C,0,3.4865818407,0.8085688794,1.0008385373\H,0,4.4838181754,0.5847243734,0.6060137202\H,0,3.367594189,1.8954592723,1.0445739008\H,0,3.4248641666,0.4276766591,2.0244838549\C,0,2.5153193671,0.7324960073,-1.3317404827\H,0,3.507816291,0.5147160498,-1.7424299946\H,0,1.7661271154,0.287401358,-1.9923655666\H,0,2.3801495298,1.8201818283,-1.340072735\C,0,2.5902928721,-1.3688201368,0.0757421925\H,0,3.5838557556,-1.6182097659,-0.3136806837\H,0,2.5046281914,-1.7960950903,1.0811484645\H,0,1.8416669437,-1.8447578298,-0.5642085338\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-617.792176\RMSD=8.292e-09\Dipole=0.2278688,-0.1392547,-1.4887621\PG=C01 [X(C10H18O3)]\\@

5a-a

1\1\GINC-CICUM88\SP\RB3LYP\6-311+G(d,p)\C8H14O2\ZIPSE\03-Jan-2006\0\\# P BECKE3LYP/6-311+G(D,P) INT=FINEGRID SCF=(DIRECT,TIGHT) GEOM=CHECK GUESS=READ\\upy42 b3lyp/6-311+G(d,p)//b3lyp/6-31G(d) sp cyclohexyl acetate\\0,1\C,0,-2.3080625404,-0.9016915422,0.2145155124\C,0,-2.2608672569,-0.9356504441,1.7498671677\C,0,-0.8359339137,-1.2048303457,2.25848371

69\C,0,0.1689190573,-0.1916642458,1.6845160018\C,0,0.1103014594,-0.175
0973103,0.1584970826\C,0,-1.3013826507,0.1104828522,-0.3589699467\H,0,
-0.8072783963,-1.1742745766,3.354502876\H,0,-2.6097855997,0.0297895683
,2.1448465858\H,0,-2.9498049394,-1.6983312342,2.1340192764\H,0,-2.0789
321201,-1.9029347271,-0.1782687932\H,0,-3.3189401433,-0.6563556008,-0.
1332456123\H,0,-0.0644998343,0.8157842535,2.0558276924\H,0,1.189169662
,-0.4247922635,2.0119399524\H,0,0.4617170416,-1.128740303,-0.249471148
6\H,0,-1.5829246371,1.1289587334,-0.0567187123\H,0,-1.3009169379,0.079
6989968,-1.453749362\H,0,-0.5336147519,-2.2214304236,1.9674273589\O,0,
1.0290763779,0.8603270547,-0.2870622333\C,0,1.5911067378,0.708865731,-
1.5084893875\O,0,1.3753632874,-0.2266109551,-2.2488527941\C,0,2.521748
5085,1.8618149639,-1.8113296687\H,0,1.9703320938,2.8074502069,-1.78349
49057\H,0,3.3083212184,1.9212002689,-1.0519000256\H,0,2.9666636145,1.7
208703505,-2.796937834\\Version=x86-Linux-G03RevB.03\State=1-A\HF=-463
.8964326\RMSD=9.334e-09\Dipole=-0.1840112,0.3839901,0.7038883\PG=C01 [
X(C8H14O2)]\\@

5b-a

1\1\GINC-CICUM85\SP\RB3LYP\6-311+G(d,p)\C9H16O2\ZIPSE\03-Jan-2006\0\\#
P BECKE3LYP/6-311+G(D,P) INT=FINEGRID SCF=(DIRECT,TIGHT) GEOM=CHECK GU
ESS=READ\\upy44_01 b3lyp/6-311+G(d,p)//b3lyp/6-31G(d) sp\\0,1\C,0,-2.6
108574037,0.9109655867,-2.0958299281\C,0,-2.6332177463,0.9911355718,-0
.5616197246\C,0,-1.2109882098,1.0564698666,0.0209864244\C,0,-0.3678089
993,-0.1218325959,-0.471841088\C,0,-0.3248038731,-0.1966871587,-1.9966
717847\C,0,-1.7462880741,-0.2636008691,-2.580356313\O,0,1.0063741207,0
.016974761,-0.0171802883\C,0,1.3054536021,-0.4557879914,1.2144874357\C
,0,2.7753229604,-0.2399613008,1.5274762971\C,0,3.1712908219,-0.7604176
901,2.907648007\O,0,0.5030807163,-0.9815486134,1.9570672362\H,0,-0.721
5739997,1.9891494838,-0.2929004562\H,0,-1.2396394647,1.0514358624,1.11
58114254\H,0,-3.1495067049,0.1075952259,-0.159033127\H,0,-3.2094465301
,1.8639453065,-0.2311825095\H,0,0.1929318909,0.694488445,-2.3775075686
\H,0,0.2662381667,-1.0667684947,-2.3066841363\H,0,-1.6963490199,-0.277
3993067,-3.6759585059\H,0,-2.2190317836,-1.2096128529,-2.2783732279\H,
0,-2.2064093127,1.849742981,-2.5020072405\H,0,-3.6318566,0.8152158722,
-2.4860823381\H,0,-0.7637695089,-1.053147416,-0.0530753201\H,0,3.36006
95191,-0.7227951001,0.7338846228\H,0,2.9823240244,0.8336107541,1.42958
17719\H,0,2.9767745429,-1.8336336742,2.9930147348\H,0,4.2365900896,-0.
5858566528,3.0910591438\H,0,2.5983975258,-0.2610801296,3.6946811925\\V
ersion=x86-Linux-G03RevB.03\State=1-A\HF=-503.2209911\RMSD=9.478e-09\D
ipole=0.1261881,0.3667585,-0.6538652\PG=C01 [X(C9H16O2)]\\@

5c-a

1\1\GINC-MORITZ\SP\RB3LYP\6-311+G(d,p)\C10H18O2\ZIPSE\03-Jan-2006\0\\#
P BECKE3LYP/6-311+G(D,P) INT=FINEGRID SCF=(DIRECT,TIGHT) GEOM=CHECK GU
ESS=READ\\upy47_01 b3lyp/6-311+G(d,p)//b3lyp/6-31G(d) sp\\0,1\C,0,-1.3
597362805,1.1149112681,1.3898511953\C,0,-1.3671537303,1.0753730311,2.9
272830946\C,0,0.0439987796,1.2713227102,3.5039393779\C,0,1.0315206575,
0.251068383,2.917062028\C,0,1.0372465043,0.2911761731,1.3795741272\C,0
,-0.3750618026,0.0939540565,0.8238737904\O,0,-0.377481122,0.2605086812
,-0.6198660062\C,0,-0.0538456054,-0.8165589795,-1.3743127027\C,0,-0.06
16583922,-0.4596669092,-2.8562644919\C,0,-0.0899557229,-1.722385561,-3
.7207050335\O,0,0.2207330091,-1.906632523,-0.9175793369\C,0,1.15433545
32,0.4339399805,-3.177792446\H,0,2.0442331307,0.4336343661,3.296275018
8\H,0,0.3921029314,2.2881945025,3.2704135119\H,0,0.0204194651,1.192485
7936,4.5979702705\H,0,-1.7646205951,0.1074120388,3.2657453358\H,0,-2.0
497492268,1.8422687728,3.3129768119\H,0,1.4135568322,1.2637913169,1.03
25247374\H,0,1.700030029,-0.4807134884,0.9740132759\H,0,-0.7127661666,
-0.9248862365,1.040449904\H,0,-1.0641641536,2.1155260546,1.0453846931\
H,0,-2.3621813124,0.9225680701,0.98929242\H,0,0.7517232649,-0.75826296
97,3.2518506163\H,0,-0.9679426009,0.1329217424,-3.0349698968\H,0,2.091
0807277,-0.108787886,-3.0045100529\H,0,1.1314691868,0.7377855814,-4.22
99893264\H,0,1.1596266971,1.3362613179,-2.5594688012\H,0,-0.9697456918
,-2.3366996662,-3.5043739499\H,0,-0.11180325,-1.4538383626,-4.78271240
91\H,0,0.7945764715,-2.33947513,-3.5363630509\\Version=x86-Linux-G03Re
vB.03\State=1-A\HF=-542.5447796\RMSD=2.777e-09\Dipole=-0.1267703,0.766
7338,0.1418931\PG=C01 [X(C10H18O2)]\\@

5d-a

1\1\GINC-MORITZ\SP\RB3LYP\6-311+G(d,p)\C11H20O2\ZIPSE\07-Jan-2006\0\\#
P BECKE3LYP/6-311+G(D,P) INT=FINEGRID SCF=(DIRECT,TIGHT) GEOM=CHECK GU
ESS=READ\\upy50_02 b3lyp/6-311+G(d,p)//b3lyp/6-31G(d) sp\\0,1\C,0,-3.2
186694177,1.1076637122,-2.6048011389\C,0,-3.2390077707,1.2972944297,-1
.0802171464\C,0,-1.8157730061,1.3524642353,-0.4996795965\C,0,-1.015947
8222,0.1122595375,-0.9054857727\C,0,-0.9750234149,-0.0730039491,-2.421
0116681\C,0,-2.3977898617,-0.129271471,-3.002295422\O,0,0.3625432314,0
.2331639911,-0.4576627018\C,0,0.6426099681,-0.1544034478,0.8074512654\
C,0,2.1072219372,0.0857920896,1.1301125072\C,0,2.6110088303,-0.6869859
286,2.3596737918\C,0,3.9943050285,-0.1728890472,2.7825700559\O,0,-0.18
02036916,-0.6066275364,1.5772051445\C,0,2.63727693,-2.2003850406,2.101
870464\H,0,-1.2929265688,2.2425507444,-0.8769581411\H,0,-1.8450065289,
1.4256426873,0.5927267121\H,0,-3.7870326987,0.4637893365,-0.617370057\
H,0,-3.7833238418,2.2116309544,-0.8143372274\H,0,-0.4247958881,0.76888
59751,-2.8634816879\H,0,-0.4163541227,-0.9841935454,-2.666012643\H,0,-
2.348052258,-0.2225254923,-4.0940120483\H,0,-2.9049513135,-1.033660995

5,-2.635542772\H,0,-2.7793791518,1.999761199,-3.0750116796\H,0,-4.2422
444678,1.0222178609,-2.9906155866\H,0,-1.4450922823,-0.7719813347,-0.4
224799588\H,0,2.7059807002,-0.1456774945,0.2403650223\H,0,2.2175735864
,1.1684146265,1.2901979861\H,0,1.9022971599,-0.4961547021,3.1755044981
\H,0,2.9750485531,-2.7416649588,2.9932462081\H,0,1.6421584596,-2.57304
77986,1.8407498732\H,0,3.325724808,-2.4476273886,1.2824967795\H,0,3.97
40913048,0.8996781365,3.0114301232\H,0,4.350780284,-0.6990344096,3.675
6566881\H,0,4.7355195427,-0.3305057591,1.9879843313\\Version=x86-Linux
-G03RevB.03\State=1-A\HF=-581.8698385\RMSD=9.974e-09\Dipole=0.0742883,
0.3291417,-0.610175\PG=C01 [X(C11H20O2)]\\@

5e-a

1\1\GINC-MORITZ\SP\RB3LYP\6-311+G(d,p)\C11H20O2\ZIPSE\04-Jan-2006\0\\#
P BECKE3LYP/6-311+G(D,P) INT=FINEGRID SCF=(DIRECT,TIGHT) GEOM=CHECK GU
ESS=READ\\upy48_01 b3lyp/6-311+G(d,p)//b3lyp/6-31G(d) sp\\0,1\C,0,-3.1
449889777,0.8820468786,-2.2483832411\C,0,-3.1510014064,1.0053942385,-0
.716846367\C,0,-1.7225362411,1.0570020928,-0.1487250455\C,0,-0.9077228
693,-0.1508605978,-0.6165823776\C,0,-0.8803699736,-0.2681758014,-2.139
1154109\C,0,-2.3082830954,-0.3222649792,-2.7078780581\O,0,0.4722584038
,-0.0268392061,-0.176514439\C,0,0.7738994559,-0.4693127467,1.067647087
7\C,0,2.2621342566,-0.2712058056,1.3877738859\C,0,3.1099689922,-1.0367
86809,0.3477362279\O,0,-0.0429361961,-0.9586887795,1.8203766743\C,0,2.
5411008072,-0.8106124836,2.7990412748\C,0,2.5909253761,1.236959465,1.3
189019001\H,0,-1.2171897569,1.9710656109,-0.4909838517\H,0,-1.74097792
32,1.0811705634,0.9460117707\H,0,-3.6817915593,0.144420703,-0.28524063
35\H,0,-3.70592545,1.8989251085,-0.4059133979\H,0,-0.3489762251,0.6018
482633,-2.5491912914\H,0,-0.3097991252,-1.1582054654,-2.430366575\H,0,
-2.2685304787,-0.3665610475,-3.8031161296\H,0,-2.7968993917,-1.2503172
142,-2.3768207857\H,0,-2.7263126837,1.8009412221,-2.6846280267\H,0,-4.
1713667929,0.7956544116,-2.6264881584\H,0,-1.3173806624,-1.0622529911,
-0.1685530734\H,0,3.600285179,-0.6750217182,3.046277096\H,0,1.93994872
78,-0.2883513666,3.549313098\H,0,2.3023502245,-1.8761354313,2.87011632
34\H,0,3.6495861408,1.3962825974,1.5549851295\H,0,2.3948263149,1.64161
76337,0.3219926414\H,0,1.9964130542,1.8055089188,2.0436840762\H,0,4.17
5544296,-0.9102775294,0.5723283404\H,0,2.8884433774,-2.1103348562,0.36
9396415\H,0,2.9244171262,-0.6688542377,-0.665120106\\Version=x86-Linux
-G03RevB.03\State=1-A\HF=-581.8680548\RMSD=7.355e-09\Dipole=0.1081835,
0.3625861,-0.7029026\PG=C01 [X(C11H20O2)]\\@

6a-a

1\1\GINC-TERMINUS\SP\RB3LYP\6-311+G(d,p)\C2H4O2\ZIPSE\24-Sep-2003\0\\#
P BECKE3LYP/6-311+G(D,P) SCF=TIGHT GEOM=CHECK GUESS=READ INT=FINEGRID\

\cpy3dxsp1 b3lyp/6-311+G(d,p)//b3lyp/6-31G(d) sp acetic acid\\0,1\C,0.1145251349,0.,-0.1060380379\C,0.050049472,0.,1.4007392685\O,1.1207546791,0.,-0.7781383217\O,-1.128750808,0.,-0.6544195254\H,-0.9940626434,0.,-1.6207891038\H,1.0610667379,0.,1.8083579894\H,-0.4952413526,-0.8820371815,1.7523432537\H,-0.4952413526,0.8820371815,1.7523432537\\Version=x86-Linux-G98RevA.7\State=1-A'\HF=-229.1645742\RMSD=3.298e-09\Dipole=-0.5702992,0.,0.3852158\PG=CS [SG(C2H2O2),X(H2)]\\@

6b-a

1\1\GINC-MORITZ\SP\RB3LYP\6-311+G(d,p)\C3H6O2\ZIPSE\03-Jan-2006\0\\#P
BECKE3LYP/6-311+G(D,P) INT=FINEGRID SCF=(DIRECT,TIGHT)
GEOM=CHECK GUES
S=READ\\upy46b b3lyp/6-311+G(d,p)//b3lyp/6-31G(d)
sp\\0,1\C,0,0.553403
4317,-0.0178601221,0.1470260745\O,0,0.5056556709,-0.1075142719,1.35371
22896\O,0,1.7284148152,0.0166669313,-0.5340479792\H,0,2.4306261116,-0.
0434245683,0.1406870046\C,0,-0.6323089679,0.0692583088,-0.7898961711\H
,0,-0.543848361,-0.7510445642,-1.5139588781\H,0,-0.5229638252,0.989849
4097,-1.3778132781\C,0,-1.9714172629,0.0282976304,-0.0569451193\H,0,-2
.7992628963,0.0954673751,-0.7701025933\H,0,-2.0789328467,-0.9001153429
,0.5116426985\H,0,-2.0562452773,0.8578715123,0.6511218585\\Version=x86
-Linux-G03RevB.03\State=1-A\HF=-268.4893189\RMSD=4.568e-09\Dipole=-0.0
228432,0.0481748,-0.6337176\PG=C01 [X(C3H6O2)]\\@

6c-a

1\1\GINC-MAX\SP\RB3LYP\6-311+G(d,p)\C4H8O2\ZIPSE\05-Dec-2005\0\\#P BEC

KE3LYP/6-311+G(D,P) SCF=TIGHT INT=FINEGRID GEOM=CHECK GUESS=READ\\upy3
2 b3lyp/6-311+G(d,p)//b3lyp/6-31G(d) sp isobutyric acid\\0,1\C,0,0.570
7763527,0.1335814495,0.5582523812\O,0,0.6971618399,-0.6730330074,1.453

3233123\O,0,1.5356472593,1.0464944983,0.2677477466\H,0,2.2629316723,0.
8753196972,0.8953777854\C,0,-0.6189295828,0.2568921664,-0.3798338951\C
,0,-1.8230275232,-0.5148018306,0.16597353\C,0,-0.2152189079,-0.2158722
666,-1.7925982672\H,0,-0.8592387706,1.3265509098,-0.4413159043\H,0,-2.
1153773888,-0.1505129918,1.1557087488\H,0,-2.6789316793,-0.4058781458,
-0.5088406218\H,0,-1.589287023,-1.5795686772,0.262502439\H,0,0.6311299
366,0.3593694367,-2.1788491079\H,0,0.0627124678,-1.2762624331,-1.78224
04127\H,0,-1.0580140415,-0.0955068349,-2.4816738912\\Version=x86-Linux
-G03RevB.03\State=1-A\HF=-307.8131518\RMSD=6.360e-09\Dipole=-0.0810364
,0.3984854,-0.5385991\PG=C01 [X(C4H8O2)]\\@

6d-a

1\1\GINC-CICUM82\SP\RB3LYP\6-311+G(d,p)\C5H10O2\ZIPSE\16-Jan-2006\0\\#
P BECKE3LYP/6-311+G(D,P) INT=FINEGRID SCF=(DIRECT,TIGHT) GEOM=CHECK GU
ESS=READ\\upy69_01 b3lyp/6-311+G(d,p)//b3lyp/6-31G(d) sp 3-methylbutyr

ic acid\\0,1\C,0,0.3693021032,0.7143103802,-
2.4497655477\C,0,0.3888879
352,0.695102347,-0.9150035256\C,0,1.827858152,0.6922277472,-
0.37847120
52\C,0,-0.4121414412,-0.5060315965,-0.3884733205\C,0,-
0.6973848523,-0.
4556046972,1.0978307561\O,0,-1.1441593477,-
1.6529864681,1.5576531074\O
,0,-0.5837072776,0.5106009178,1.820466096\H,0,-1.331184735,-
1.52214782
41,2.5065841235\H,0,0.0947209195,-1.4532965308,-
0.6133373101\H,0,-1.38
87357138,-0.5669616533,-0.8904335706\H,0,-
0.1068932942,1.6027148053,-0
.5475473605\H,0,-0.654823627,0.7624979989,-
2.8394050223\H,0,0.91608608
11,1.5817949438,-2.8364561448\H,0,0.8419704683,-
0.1861609211,-2.863465

1768\H,0,1.8431326805,0.7189216424,0.7152744314\H,0,2.36889455
39,-0.20
42611774,-0.7102398567\H,0,2.3806342879,1.5659580342,-
0.7426306821\\Ve
rsion=x86-Linux-G03RevB.03\State=1-A\HF=-
347.1380636\RMSD=2.612e-09\Di
pole=-0.0627377,-0.397906,-0.3904943\PG=C01 [X(C5H10O2)]\\@

6e-a

1\1\GINC-PIRX\SP\RB3LYP\6-311+G(d,p)\C5H10O2\ZIPSE\05-Dec-
2005\0\\#P B
ECKE3LYP/6-311+G(D,P) SCF=TIGHT INT=FINEGRID GEOM=CHECK
GUESS=READ\\up
y21 b3lyp/6-311+G(d,p)//b3lyp/6-31G(d) sp pivalic
acid\\0,1\C,0,0.7082

731976,0.0679685048,0.6478775297\O,0,0.7110793606,0.5767061543
,1.74774
32544\O,0,1.8182533862,-
0.5319990936,0.1385781214\H,0,2.505788392,-0.4
395382099,0.8246363211\C,0,-0.4769354889,0.0094148987,-
0.3171777621\C,
0,-0.0878553459,0.7267624805,-1.629659714\C,0,-0.8085701446,-
1.4711808
912,-0.6111743019\C,0,-
1.6813567773,0.706051774,0.3339108389\H,0,0.166
3920517,1.7773115247,-
1.4473069907\H,0,0.7687627228,0.2445812649,-2.10
90527146\H,0,-0.933320501,0.7021813361,-2.3267566091\H,0,-
1.074815441,
-2.0079630798,0.3067177668\H,0,-1.6645544226,-1.5278420475,-
1.29340598
12\H,0,0.0377071034,-1.9848981817,-1.0759541347\H,0,-
2.5409569636,0.67
32974595,-0.3450565478\H,0,-
1.9621724739,0.2180341366,1.2721294997\H,0
,-1.458825088,1.7530787106,0.5608188401\\Version=x86-Linux-
G03RevB.03\
State=1-A\HF=-347.1366776\RMSD=6.710e-09\Dipole=-0.0131701,-
0.2842305,
-0.6227025\PG=C01 [X(C5H10O2)]\\@