Supporting Information

Mechanistic Studies on Alcoholysis of α-Keto esters

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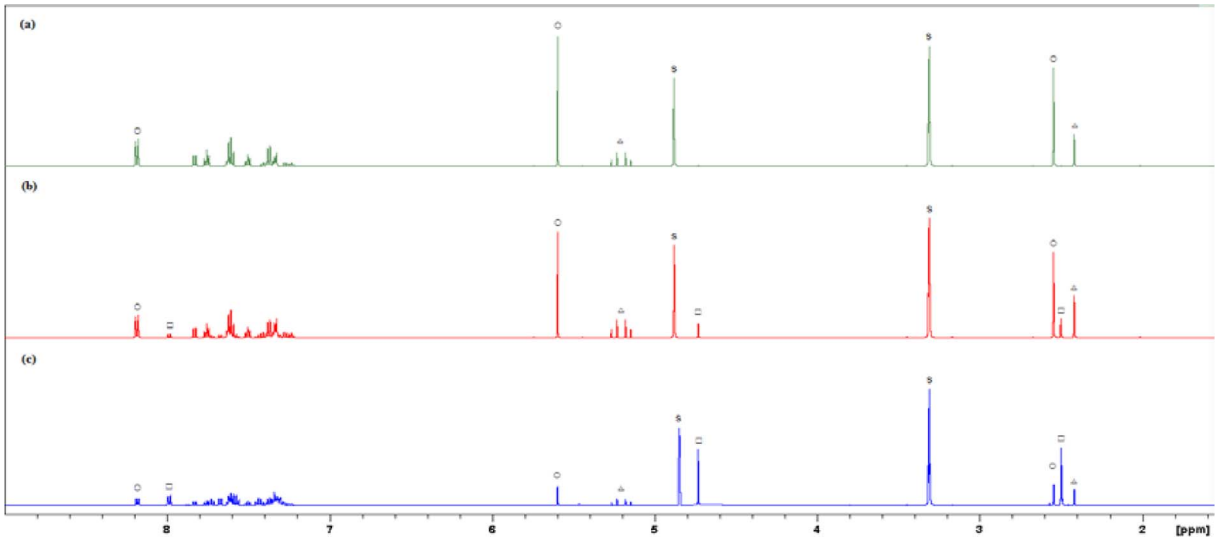

Figure 1. ^{1}H NMR Spectra of 2-Methylphenacyl Phenylglyoxylate (**1a**) in Methanol-d_4 (a) Immediately After the Sample Preparation, (b) After 2 Hours, and (c) After 24 Hours: ○ = Keto ester, △ = Hemiacetal, □ = Phenacyl Alcohol, s = Solvent Peaks.

Table 1. Concentrations of S, H, and A, and the corresponding time derivatives measured in time for the reaction of **3a**

Time (sec)	[S]	[H]	[A]	d[S]/dt	d[H]/dt	d^2[A]/dt^2	d^2[S]/dt^2	d^2[H]/dt^2
0	0.014	0	0	-2.73×10^{-6}	1.25×10^{-5}	1.25×10^{-10}	2.22×10^{-9}	-1.04×10^{-8}
600	0.0124	0.0075	0	-1.40×10^{-6}	6.25×10^{-6}	7.12×10^{-11}	1.20×10^{-9}	-5.69×10^{-9}
7200	0.012	0.0074	9.90×10^{-4}	-1.93×10^{-7}	-1.18×10^{-7}	2.11×10^{-12}	9.13×10^{-11}	-4.84×10^{-10}
10800	0.0108	0.0066	0.00182	-1.94×10^{-7}	-1.31×10^{-7}	-1.02×10^{-11}	6.37×10^{-12}	3.01×10^{-12}
21600	0.0101	0.0063	0.00241	-5.36×10^{-8}	-2.92×10^{-8}	-3.46×10^{-12}	6.41×10^{-12}	4.58×10^{-12}
67200	0.0083	0.0051	0.00578	-6.22×10^{-8}	-3.96×10^{-8}	3.34×10^{-13}	-4.31×10^{-14}	8.83×10^{-14}
79200	0.0073	0.0045	0.00680	-6.10×10^{-8}	-3.47×10^{-8}	-7.88×10^{-13}	1.25×10^{-12}	9.21×10^{-13}
93600	0.0068	0.0043	0.00798	-2.66×10^{-8}	-1.40×10^{-8}	-1.13×10^{-12}	1.21×10^{-12}	7.13×10^{-13}
153000	0.0057	0.0035	0.00976	-2.52×10^{-8}	-1.46×10^{-8}	-1.20×10^{-13}	-9.14×10^{-14}	-2.76×10^{-14}
192600	0.0044	0.0028	0.01132	-3.33×10^{-8}	-1.64×10^{-8}	1.19×10^{-13}	-2.06×10^{-13}	-4.57×10^{-14}

Unit of concentration is mol/L

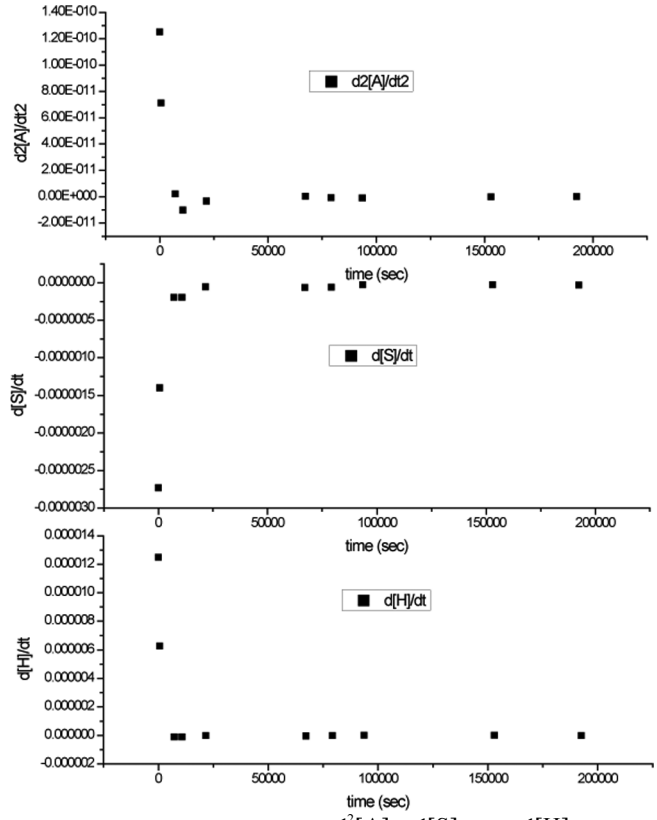

Figure 2. Time dependence of $\frac{d^2[A]}{dt^2}$, $\frac{d[S]}{dt}$ and $\frac{d[H]}{dt}$ plotted from the data in Table 1.

Table 2. Kinetic data of methanolysis of α-keto esters

Compounds	k_1	k_{-1}	k_2	k_{obs}
1a	7.9×10^{-4}	8.0×10^{-4}	4.1×10^{-5}	4.0×10^{-5}
1b	6.1×10^{-4}	1.3×10^{-3}	3.4×10^{-4}	1.6×10^{-4}
1c	1.7×10^{-4}	1.2×10^{-3}	2.3×10^{-3}	1.1×10^{-4}
1d	1.6×10^{-4}	4.4×10^{-5}	9.1×10^{-6}	3.3×10^{-5}
1e	1.4×10^{-4}	1.4×10^{-4}	9.1×10^{-6}	8.6×10^{-6}
2a	4.3×10^{-5}	6.5×10^{-6}	5.2×10^{-6}	3.5×10^{-5}
2b	1.2×10^{-3}	1.9×10^{-3}	3.7×10^{-5}	2.4×10^{-5}
3a	2.0×10^{-4}	6.2×10^{-4}	2.1×10^{-5}	6.6×10^{-6}
3b	2.3×10^{-4}	3.2×10^{-4}	1.5×10^{-4}	1.1×10^{-4}