Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

A further study of acetylacetone nitrosation

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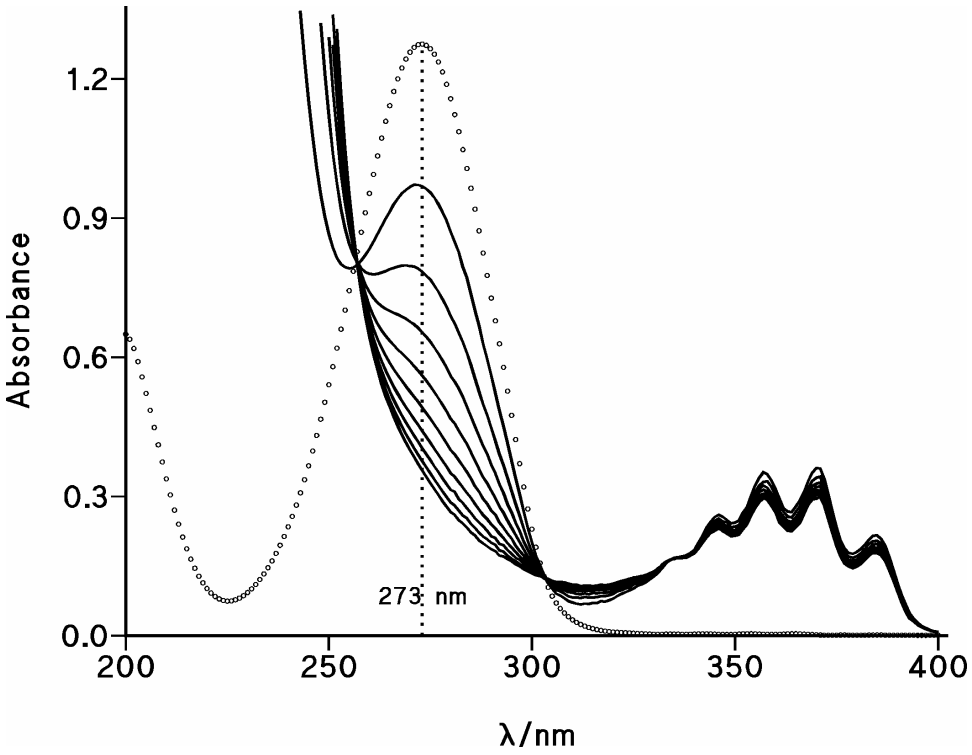

Figure S1. Reaction spectra (scans at 2 min interval) for the nitrosation of AcAc at [nit]=6.5 mM, [AcAc]=0.68 mM, and $[H^+]$=0.10 M ($HClO_4$) showing the decreasing absorption due to the enol consumption at 273 nm, and the HNO_2-system band between 300-4oo nm. (o)AcAc spectrum recorded in the absence of nit under the same experimental conditions of the reaction.

Table S1. The pseudo first-order rate constants measured in the nitrosation of AcAc as a function of the buffer monocloroacético-monocloroacetato concentration; [AcAc]=0.2 mM, [nit]=5.8 mM and I=0.34 M ($NaClO_4$)

[buffer]/M	pH	$k_{obs}/10^{-4}s^{-1}$	[buffer]/M	pH	$k_{obs}/10^{-4}s^{-1}$	[buffer]/M	pH	$k_{obs}/10^{-4}s^{-1}$
0,60	2,57	2,71	0,57	2,79	2,16	0,60	2,66	2,61
0,53	2,57	2,66	0,52	2,78	2,16	0,53	2,65	2,60
0,47	2,56	2,61	0,47	2,77	2,14	0,47	2,65	2,51
0,40	2,56	2,52	0,40	2,78	2,03	0,40	2,65	2,48
0,33	2,56	2,50	0,33	2,77	2,03	0,33	2,65	2,37
0,27	2,56	2,41	0,27	2,73	2,17	0,27	2,66	2,23
0,20	2,56	2,24	0,20	2,72	2,11	0,20	2,66	2,15
0,17	2,56	2,23	0,13	2,73	2,03	0,13	2,66	2,07
0,13	2,56	2,15	0,10	2,73	1,98	0,067	2,68	1,90

Table S2. The pseudo first-order rate constants measured in the nitrosation of AcAc as a function of the buffer concentration at the indicated experimental conditions.

Buffer dichloroacetic/dichloroacetate; [AcAc]=0.21 mM; [nit]=6.67 mM; I=0.35 M			Buffer trichloroacetic / trichloroacetate; [AcAc]=0.21 mM; [nit]=6.67 mM; I=0.50 M		
[buffer]/M	pH	$k_{obs}/10^{-3}\ s^{-1}$	[buffer]/M	$[H^+]$/M	$k_{obs}/10^{-3}\ s^{-1}$
0.54	1.46	1.65	0.53	0.37	6.65
0.54	1.30	2.135	0.53	0.22	5.44
0.54	1.14	2.71	0.50	0.31	5.77
0.47	1.27	2.09	0.50	0.20	4.75
0.40	1.30	1.96	0.50	0.11	3.67
0.33	1.33	1.79	0.42	0.11	3.31

Table S3. The pseudo first-order rate constants measured in the nitrosation of AcAc as a function of the perchloric acid concentration at the indicated experimental conditions.

I variable; [AcAc]=0.27 mM; [nit]=8.33 mM			I=0.30 M; [AcAc]=0.21 mM; [nit]=6.67 mM		
$[H^+]$/M	$k_{obs}/10^{-3}\ s^{-1}$	$k_o/mol^{-1}dm^3s^{-1}$	$[H^+]$/M	$k_{obs}/10^{-3}\ s^{-1}$	$k_o/mol^{-1}dm^3s^{-1}$
0.217	5.41	0.649	0.217	4.89	0.733
0.183	4.79	0.575	0.183	4.52	0.678
0.150	4.125	0.495	0.150	3.905	0.585
0.117	3.44	0.413	0.117	3.25	0.487
0.100	3.00	0.360	0.100	2.91	0.436
0.083	2.54	0.305	0.083	2.51	0.376
0.067	2.13	0.256	0.067	2.06	0.309
0.050	1.55	0.186	0.050	1.56	0.234
0.033	1.045	0.125	0.033	1.09	0.163
0.025	0.764	0.092	0.025	0.82	0.123
0.017	0.523	0.063	0.017	0.55	0.0825