Supplementary Material (ESI) for Chemical Communications

Supplementary information

Optical fiber-based on-line UV/Vis spectroscopic monitoring of chemical reaction kinetics under high pressure in a capillary microreactor

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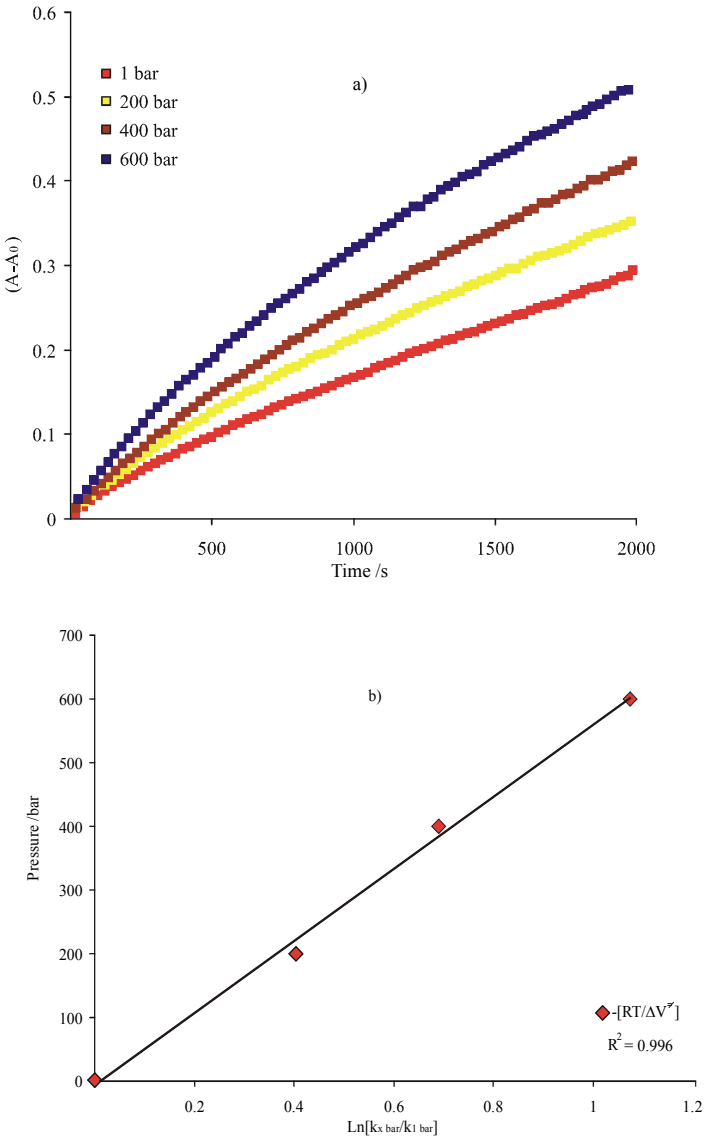

Fig. 1 a) Plot of the change of the absorbance at 391 nm versus time (10 sec intervals) for the product **3b** formation of the reaction of 1-chloro-4-nitrobenzene (**1b)** with pyrrolidine (**2a**) under different pressures (1-600 bar). b) Plot of the pressure versus the logarithm of the rate constants for the same reaction to calculate $\Delta V^{\neq}$ using eqn. 2.

Table 1 Rate constants for the nucleophilic aromatic substitution reaction of halonitrobenzenes **1** with amines **2**.

1[a]	**2**[a]	P /bar	k_{obs} /s^{-1}	k /M^{-1} s^{-1}
1a	**2a**	1	1.40×10^{-02}	1.12×10^{-02}
		100	1.78×10^{-02}	1.42×10^{-02}
		320	3.24×10^{-02}	2.59×10^{-02}
		440	3.86×10^{-02}	3.09×10^{-02}
1b	**2a**	1	2.47×10^{-04}	1.97×10^{-04}
		200	3.50×10^{-04}	2.80×10^{-04}
		400	4.89×10^{-04}	3.92×10^{-04}
		600	6.95×10^{-04}	5.56×10^{-04}
1c	**2a**	1	3.75×10^{-04}	3.00×10^{-04}
		200	4.92×10^{-04}	3.94×10^{-04}
		400	2.03×10^{-03}	1.62×10^{-03}
		600	8.25×10^{-04}	6.60×10^{-04}
1a	**2b**	1	4.89×10^{-03}	3.91×10^{-03}
		200	6.53×10^{-03}	5.22×10^{-03}
		400	8.40×10^{-03}	6.72×10^{-03}
		600	1.10×10^{-02}	8.80×10^{-03}
1b	**2b**	1	2.09×10^{-04}	1.67×10^{-04}
		200	2.52×10^{-04}	2.02×10^{-04}
		400	3.22×10^{-04}	2.57×10^{-04}
		600	3.62×10^{-04}	2.89×10^{-04}
1c	**2b**	1	2.11×10^{-05}	1.69×10^{-05}
		200	2.37×10^{-05}	1.90×10^{-05}
		400	2.78×10^{-05}	2.22×10^{-05}
		600	3.22×10^{-05}	2.57×10^{-05}
1a	**2c**	1	5.62×10^{-05}	4.49×10^{-05}
		200	7.01×10^{-05}	5.61×10^{-05}
		400	8.24×10^{-05}	6.59×10^{-05}
		600	9.87×10^{-05}	7.89×10^{-05}
1b	**2c**	1	4.21×10^{-05}	3.37×10^{-05}
		200	4.96×10^{-05}	3.97×10^{-05}
		400	5.66×10^{-05}	4.53×10^{-05}
		600	6.76×10^{-05}	5.41×10^{-05}
1c	**2c**	1	1.52×10^{-07}	1.21×10^{-07}
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		600	2.17×10^{-07}	1.74×10^{-07}

[a] Upon mixing 0.125 M halonitrobenzene **1** and 1.25 M amine **2**

Table 2 Rate constants and activation volumes for the base-catalyzed reaction of 1-fluoro-4-nitrobenzene (**1a**) with pyrrolidine (**2a**) and piperidine (**2b**)

Amine	[Amine] /M	P /bar	$k/M^{-1}s^{-1}$	$\Delta V^{\neq}/cm^3mol^{-1}$	Amine	[Amine]/M	P/bar	$k/M^{-1}s^{-1}$	$\Delta V^{\neq}/cm^3mol^{-1}$
2a	1.2500	1	1.123×10^{-02}	-58.0	**2b**	1.2500	1	3.91×10^{-03}	-32.4
		100	1.424×10^{-02}				200	5.22×10^{-03}	
		320	2.591×10^{-02}				400	6.72×10^{-03}	
		440	3.086×10^{-02}				600	8.80×10^{-03}	
	0.6250	1	4.37×10^{-03}	-59.1		0.6250	1	1.95×10^{-03}	-33.4
		100	5.36×10^{-03}				200	2.50×10^{-03}	
		200	7.15×10^{-03}				400	3.35×10^{-03}	
		300	8.94×10^{-03}				600	4.43×10^{-03}	
	0.3125	1	2.83×10^{-03}	-58.1		0.3125	1	1.11×10^{-03}	-33.0
		200	4.94×10^{-03}				200	1.44×10^{-03}	
		400	7.23×10^{-03}				400	1.84×10^{-03}	
		600	1.20×10^{-03}				600	2.54×10^{-03}	
	0.1563	1	3.45×10^{-04}	-58.0		0.0325	1	1.88×10^{-04}	-32.2
		--	--				200	2.85×10^{-04}	
		320	7.48×10^{-04}				400	3.41×10^{-04}	
		440	9.90×10^{-04}				600	4.14×10^{-04}	

[a] Concentration **1a** upon mixing 0.125 M