

Table 2. Effect of varying [BAB] and [aryloximes]_o on the reaction rate at 303 K.

10^4 [BAB] (mol dm ⁻³)	10^3 [aryloximes] _o (mol dm ⁻³)	$10^4 k$ (s ⁻¹)				
		- OH	-OCH ₃	-H	-Br	-NO ₂
0.4	2.0	9.74	8.93	7.19	4.56	3.82
0.9	2.0	9.76	8.97	7.15	4.54	3.87
1.8	2.0	9.75	8.95	7.18	4.52	3.85
2.5	2.0	9.72	8.94	7.16	4.53	3.86
3.6	2.0	9.73	8.96	7.14	4.50	3.83
1.8	0.5	3.73	3.24	3.01	1.84	1.59
1.8	1.0	6.82	5.31	4.81	3.48	2.17
1.8	2.0	9.75	8.95	7.18	4.52	3.85
1.8	3.0	11.8	10.3	8.89	7.80	4.74
1.8	4.0	15.1	13.9	12.4	9.99	6.28

[HClO₄] = 1.6×10^{-4} mol dm⁻³; [RuCl₃] = 16.0×10^{-6} mol dm⁻³ at 303 K.

Table 3. Effect of varying [HClO₄] and [RuCl₃] on the reaction rate at 303 K.

10^4 [HClO ₄] (mol dm ⁻³)	10^6 [RuCl ₃] (mol dm ⁻³)	$10^4 k$ (s ⁻¹)				
		- OH	-OCH ₃	-H	-Br	-NO ₂
0.4	16.0	15.1	14.2	12.5	8.84	7.43
0.8	16.0	12.5	10.4	9.43	6.45	5.14
1.6	16.0	9.75	8.95	7.18	4.52	3.85
2.4	16.0	7.95	6.14	5.45	3.60	2.80
3.2	16.0	5.90	5.10	4.70	3.10	2.30
16.0	4.0	5.12	4.45	2.59	2.55	1.82
16.0	8.0	7.43	6.72	4.85	3.63	2.94
16.0	16.0	9.75	8.95	7.18	4.52	3.85
16.0	24.0	12.1	11.7	11.3	5.65	4.59
16.0	32.0	15.5	14.4	12.6	6.40	5.20

[BAB] = 1.8×10^{-4} mol dm⁻³; [aryloximes] = 2.0×10^{-3} mol dm⁻³ at 303 K.

Table 4. Effect of varying temperature on the reaction rate and activation parameters for the oxidation of aryloximes by BAB in presence and absence of RuCl₃.

Temperature (K)	$k' \times 10^4 / s^{-1}$				
	-OH	-OCH ₃	-H	-Br	-NO ₂
293	4.42 (0.96)	4.14(0.87)	3.62(0.70)	2.25(0.43)	1.49(0.35)
298	6.92(1.35)	6.12(1.35)	5.41(1.04)	3.28(0.63)	2.47(0.49)
303	9.75(1.76)	8.95(1.76)	7.18(1.38)	4.52(0.85)	3.85(0.72)
308	12.9(2.72)	12.6(2.72)	10.4(2.07)	7.20(1.26)	6.26(1.08)
313	18.2(3.51)	17.5(3.51)	14.9(2.76)	9.34(1.74)	8.51(1.48)
E_a (kJ mol ⁻¹)	35.2(53.6)	42.5(53.6)	46.7(55.9)	53.0(59.7)	56.5(64.2)
ΔH^\ddagger (kJ mol ⁻¹)	32.7(51.1)	39.9(51.1)	44.2(53.4)	50.5(57.1)	53.9(61.6)
ΔG^\ddagger (kJ mol ⁻¹)	91.8(96)	92.0(96.0)	92.4(96.6)	93.6(97.8)	94.1(97.0)
ΔS^\ddagger (JK ⁻¹ mol ⁻¹)	-195(-148)	-171(-148)	-159(-142)	-142(-133)	-132(-120)

[BAB] = 1.80×10^{-4} mol dm⁻³; [aryloximes] = 2.0×10^{-3} mol dm⁻³; [HClO₄] = 1.6×10^{-4} mol dm⁻³; [RuCl₃] = 16.0×10^{-6} mol dm⁻³. Values in parentheses refer to the reaction in absence of RuCl₃ catalyst. Experimental conditions are same as above without RuCl₃ catalyst.

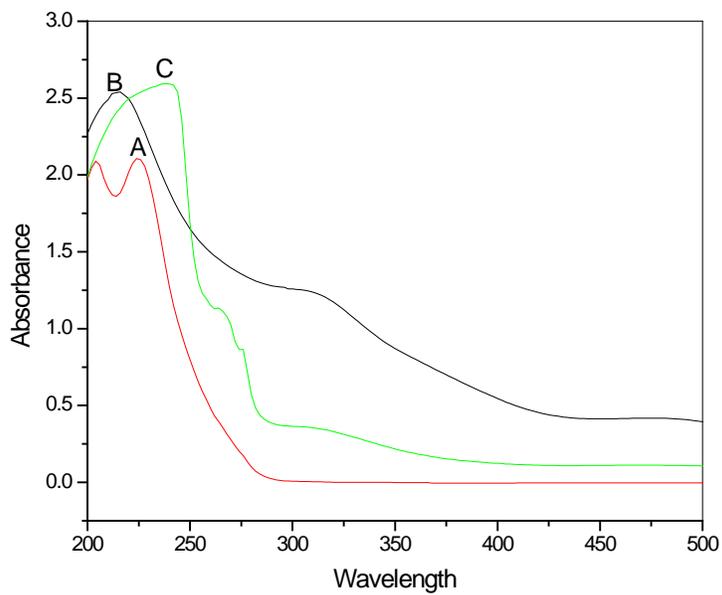


Fig. 1. UV-visible spectra of (A) RuCl₃, (B) BAB, (C) Mixture of RuCl₃ and BAB in HClO₄ medium.

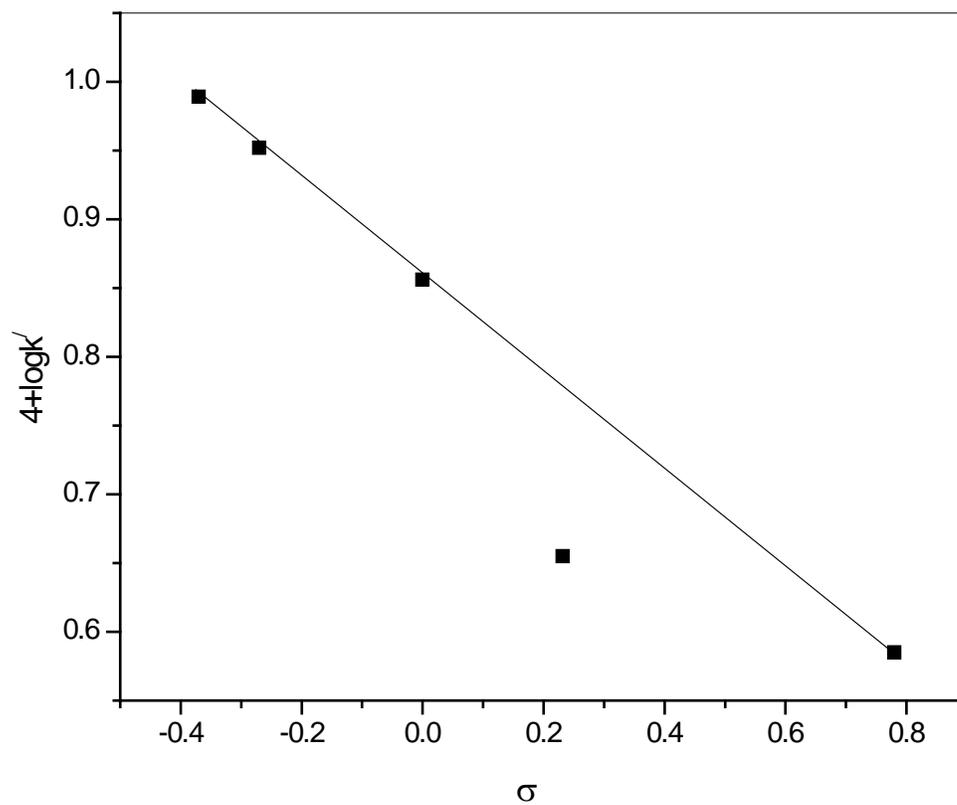


Fig. 2. Hammett plot of $\log k'$ versus σ .

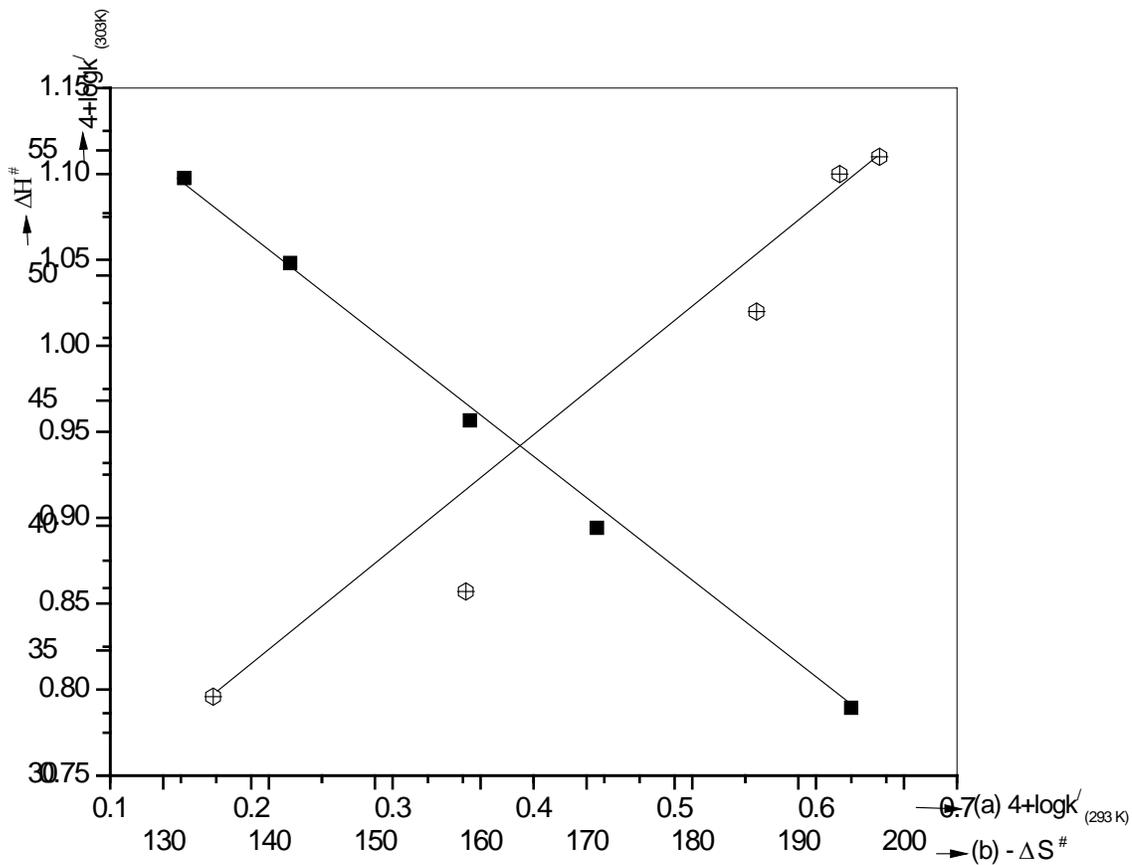
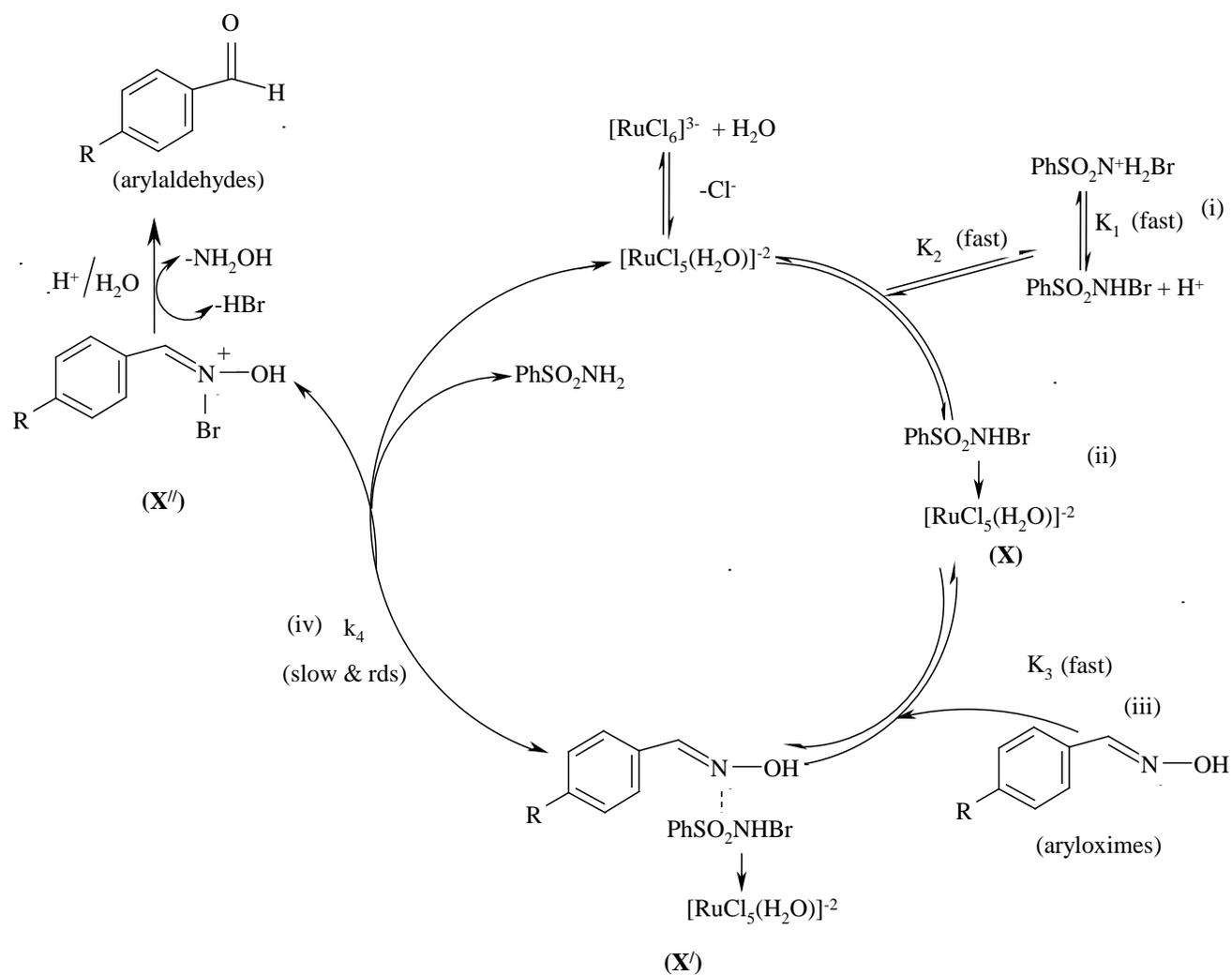


Fig. 3. Isokinetic plots of (a). $\log k'_{(293K)}$ versus $\log k'_{(303K)}$ (b). ΔH^\ddagger versus ΔS^\ddagger .



Scheme 2. A detailed proposed mechanism for RuCl_3 catalyzed oxidative conversion of aryloximes to arylaldehydes with BAB in acid medium.