-1- -2- -3,1

(2012 / 4/ 9 2012/ 3 /6)

-1- -2- -3,1
 (a3) (a2) (a1)
 (a7) (a6) (a5) (a4)

(a5 > a3 > a2 > a1 > a4)

(a1 > a7 > a6)

Kinetics and Mechanistic Studies of the Bromination of some Derivatives of 1,3-diaryl-2-propen-1-one

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ABSTRACT

The rate of bromination of 1,3-diaryl -2-propen-1-one (a1) and its derivatives p-bromo acetophenone (a2), p-chloro acetophenone (a3), p-methoxy acetophenone (a4), p-nitro acetophenone (a5), p-chloro benzaldehyde (a6) and p-nitro benzaldehyde (a7) had been studied in chloroform. The study indicated first order dependence on each of reactants with

rates ($a_5 > a_3 > a_2 > a_1 > a_4$) and ($a_1 > a_7 > a_6$) at any temperature. The effect of substituents on the rate showed that electronic factors, inductive and conjugative effects play a reasonable role on the stability of the intermediates. Suggested mechanisms, which are consistent with the results have been postulated and suitable rate laws in consonance with the suggested mechanisms have been derived.

Keywords: Bromination, Chalcones.

.(Dabbagh *et al.*, 2004)

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Furniss *et al.*, 1989 ; Pavia *et al.*, 2011; Ahmed *et al.*, 2007 ; Azarifar *et al.*, 2002 ; Bhaskar *et al.*, 2011 ; Jayapal *et al.*, 2011; Patil *et al.*, 2011).

(Freeman, 1975 ; Dabbagh *et al.*, 2000).

-2-

-3,1

-1-

)

.Chem Supply

.(

BDH

(a1-a7)

(410-496 nm)

(1×1×5 cm)

(Shimadzu, 1800)

(4.5×10^{-2} M)

(2 mL)

:

(0.9×10^{-2} M)

(1 mL)

1:10

75%

 (A_{∞}) $(283-303^{\circ}\text{K})$

()

$$r = k_{obs} [Br_2] \dots\dots\dots (1)$$

 k [reactant] k_{obs} $(\epsilon_{\max} = 361.12 \text{ M}^{-1} \text{ cm}^{-1}) (408 \text{ nm})$

(charge transfer complex)

$(\lambda_{\text{max}} = 410 - 422)$

$(\lambda_{\text{max}} = 496)$

.(2)

(1)

$$\ln \frac{A_0 - A_\infty}{A_t - A_\infty} = k_{\text{obs}} t \dots\dots\dots(2)$$

$$[\text{Br}]_0 \qquad \qquad \qquad [A_0 - A_\infty]$$

$[A_t - A_\infty]$

.(1) 298°K (a1 – a7)

298°K (a1 – a7) :1

.(3) (2)

$$\frac{1}{[A_t - A_\infty]} = \frac{1}{[A_0 - A_\infty]} + k t \dots\dots\dots(3)$$

.....

298°K (1:1) (a3) :2

(283-303°K)

.(1)

k_{obs}

(:)

(1:10)

(1: 5)

.(k = k_{obs}/[chalcone]₀)

σ

(standard deviation)

:1

(:)	1:10		1:5		1:5		1:5		1:10		1:10		1:10	
	a1		a2		a3		a4		a5		a6		a7	
	p-H		p-Br		p-Cl		p-OCH ₃		p-NO ₂		p'-Cl		p'-NO ₂	
°K /	10 ³ k _{obs} /s ⁻¹ ±	10 ⁴ k / M ⁻¹ s ⁻¹	10 ³ k _{obs} /s ⁻¹ ±	10 ⁴ k / M ⁻¹ s ⁻¹	10 ³ k _{obs} /s ⁻¹ ±	10 ⁴ k / M ⁻¹ s ⁻¹	10 ³ k _{obs} /s ⁻¹ ±	10 ⁴ k / M ⁻¹ s ⁻¹	10 ³ k _{obs} /s ⁻¹ ±	10 ⁴ k / M ⁻¹ s ⁻¹	10 ³ k _{obs} /s ⁻¹ ±	10 ⁴ k / M ⁻¹ s ⁻¹	10 ³ k _{obs} /s ⁻¹ ±	10 ⁴ k / M ⁻¹ s ⁻¹
	10 ³ σ* / s ⁻¹		10 ³ σ* / s ⁻¹		10 ³ σ* / s ⁻¹		10 ³ σ* / s ⁻¹		10 ³ σ* / s ⁻¹		10 ³ σ* / s ⁻¹		10 ³ σ* / s ⁻¹	
283	0.204 ± 0.005	0.68	2.399 ± 0.003	3.99	1.437 ± 0.009	2.40	----- -	----- -	1.439 ± 0.003	4.80	----- -	----- -	----- -	----- -
288	0.377± 0.006	1.25	3.073 ± 0.010	5.12	3.478 ± 0.003	5.80	0.809 ± 0.005	1.35	2.416 ± 0.007	8.05	----- -	----- -	0.599 ± 0.010	1.99
293	1.026 ± 0.003	3.42	5.714 ± 0.001	9.52	7.533 ± 0.008	12.56	2.009 ± 0.001	3.35	4.146 ± 0.002	13.82	0.982 ± 0.003	3.27	1.159 ± 0.004	3.86
298	2.049 ± 0.009	6.83	10.706 ± 0.001	17.84	13.108 ± 0.003	21.85	4.096 ± 0.004	6.83	6.687 ± 0.002	22.29	1.862 ± 0.008	6.21	1.974 ± 0.006	6.58
303	3.941 ± 0.003	13.14	----- -	----- -	----- -	----- -	8.179 ± 0.002	13.63	13.527 ± 0.001	45.09	4.098 ± 0.003	13.66	3.606 ± 0.002	12.02
308	----- -	----- -	----- -	----- -	----- -	----- -	----- -	----- -	----- -	----- -	7.482 ± 0.006	24.94	5.567 ± 0.001	18.56

σ *

Ln k

.(2)

.(3)

:2

	Ea / k J.mol ⁻¹	A-factor / M ⁻¹ s ⁻¹	-ΔS [‡] ₂₉₈ / J. mol ⁻¹ .K ⁻¹
a1	108.605	21.56×10 ⁸	74.55
a2	71.425	×10 ⁶ 16.11	115.23
a3	107.018	× 10 ⁷ 42.69	88.13
a4	111.134	×10 ⁹ 6.05	65.93
a5	78.321	39.02× 10 ⁶	107.89
a6	103.251	24.62×10 ⁷	92.60
a7	82.581	58.80× 10 ⁶	104.57

.....

(a1 – a7)

:3

:

C=C

(-CN , -CO₂R , -CO₂H , -

.(Smith and March, 2007)

C=C

COR)

C=C

.(Smith and March, 2007)

(a1 – a7)

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(a4)

(4)

(a1)

:

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(p-NO₂ > p-Cl > p-Br > p-H > p-OCH₃) (p-H > p-NO₂ > p-Cl)

(a5 > a3 > a2 > a1 > a4) (a1 > a7 > a6)

(a7- a1)

(111 – 78)

(a7 – a1)

(2)

.()

 $\Delta S^{\ddagger}$.(2010) (activated complex)

(a1)

(a4)

 $\Delta S^{\ddagger}$

.....

.(a1)

 $\Delta S^\ddagger$

(a4)

.(2) (a1)

(a4)

(a2 a3 a5)

(a1 a4)

.(a1)

(a2 , a3 , a5)

(2)

(a1 , a4)

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(B) (1:1)

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