Monatshefte für Chemie 109, 451—454 (1978)

Monatshefte für Chemie

Kinetics and Mechanism of the Bromination of Crotonic Acid by N-Bromosuccinimide

By

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(Received May 16th, 1977)

The bromination of crotonic acid by N-bromosuccinimide (*NBS*) is first order with respect to crotonic acid and zero order with respect to *NBS* and the rate of the reaction changes linearly with hydrogen ion concentration. The thermodynamic parameters have also been calculated.

Kinetics of bromination of olefinic compounds was first studied by *Herz* and *Mylius*[1]. *Roberts* and *Kimball*[2] have showed that the electrophilic attack by the halogen is the rate determining step. *Mortan* and *Robertson*[3], *Hartman* and *Robertson*[4] have studied the kinetics of halogen addition to α,β-unsaturated acids and nitro cinnamic acid.

The present work deals with bromination of crotonic acid by N-bromosuccinimide which has not been studied till now.

Materials and Methods

Material: N-bromosuccinimide (*NBS*) was standardised iodometrically[5]. Other chemicals used were chemically pure reagents.

Product Study and Stoichiometry

Two equivalents of *NBS* are used for one mole of crotonic acid; 750 mg of *NBS* were dissolved in least amount of distilled water and 178 mg of crotonic acid dissolved in equal amount of distilled water. The mixed solutions were left half an hour. The reaction mixture was poured in ice cold water, stirred continuously and then filtered.

The remaining solid substance is identified as dibromo-crotonic acid (m. p. 86°) by co-chromatography using silica gel G plates and benzene—methanol—acetic acid[7].

Rate measurement: The reaction was initiated by mixing the reactant solutions previously brought to thermal equilibrium in a thermostat bath. The rate was measured by pouring the reaction mixture in 5 ml of 20% KI solution. The liberated iodine was titrated against $Na_2S_2O_3$.

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0026-9247/78/0109/0451/$ 01.00

Results and Discussion

The reaction has a zero order dependence in $[NBS]$ as indicated by the linear plots of $[NBS]$ against time under experimental conditions, Table 1.

Table 1
[Crotonic acid] = $1.00 \times 10^{-3} M$
[Acetic acid] = $34.8 \times 10^{-2} M$

Temp., °C	$[NBS] \times 10^3 M$	$k_s \times 10^5$ mol · min^{-1}
20	0.50	2.97
	0.90	2.80
	2.00	2.57
15	0.70	1.43
	1.00	1.14
	1.50	1.10
	2.00	1.11
10	0.50	0.45
	0.70	0.46
	1.00	0.49

The value of k_s is obtained by multiplying the zero order rate constant by strength of hypo divided by the volume of reaction mixture taken each time for titration. The reaction has a first order dependence in crotonic acid which is shown in Table 2.

Table 2
$[NBS]$ = $1.00 \times 10^{-3} M$
[Acetic acid] = $34.8 \times 10^{-2} M$

Temp., °C	[Crotonic acid] $\times 10^3 M$	$k_s \times 10^5$ mol · min^{-1}	$\frac{k_s}{[\text{Crotonic acid}]} \times 10^2$
20	0.40	1.03	2.58
	0.80	2.05	2.57
	0.90	2.31	2.52
	1.10	2.77	2.57
	1.20	2.92	2.43
15	0.40	0.44	1.10
	0.80	0.89	1.11
	0.90	0.99	1.10
	1.10	1.20	1.09
	1.20	1.30	1.08

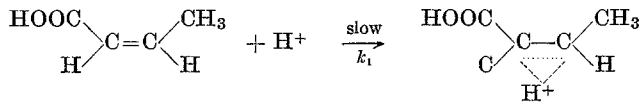
The third column in above table indicates that k_s/[crotonic acid] is fairly constant which shows the reaction a first order dependence on crotonic acid. The velocity of the reaction varies linearly with [free acid]. Table 3 shows the values of thermodynamical parameters for this reaction.

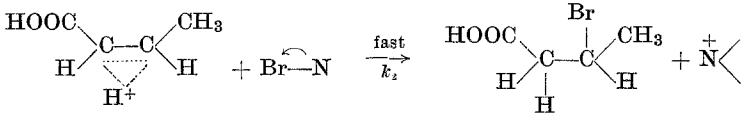
Table 3
Temp. 20 °C

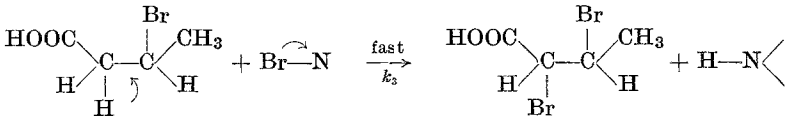
k	8.30×10^7 mol/sec
ΔE	34.8 kcal/mol
ΔS	30.3 e.u.
A	7.02×10^9 cc mol^{-1} sec^{-1}
ΔF	25.9 kcal/mol

Considering the zero order and first order dependence of the reaction in *NBS* and crotonic acid respectively and linear accelerating effect of H^+ the following mechanism is proposed:

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$







$$CH_3COO^- + N^+ \langle \rightarrow CH_3COON \langle$$

The final rate expression can be written as follows:

$$-\frac{d\,[NBS]}{dt} = k_1 \cdot [\text{crotonic acid}] \cdot [H^+]$$

This rate expression is in accord with the observed experimental facts.

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