

KINETICS AND MECHANISM OF OXIDATION OF ACETOPHENONE BY N-BROMOSUCCINIMIDE IN PERCHLORIC ACID MEDIA

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ABSTRACT

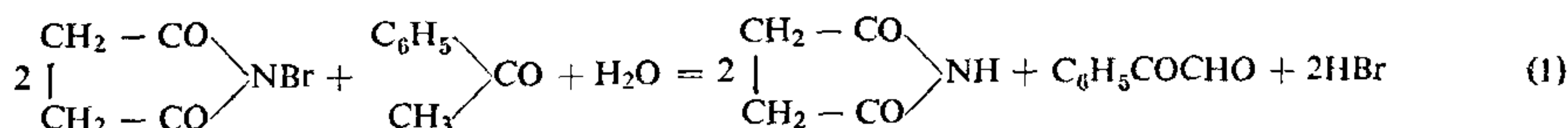
Kinetic studies on the oxidation of acetophenone by N-bromosuccinimide investigated in perchloric acid media, showed a zero order dependence to [NBS] and a first order dependence to [PhCOMe] and [H⁺]. Variation in ionic strength, mercuric acetate and succinimide do not have any effect on the reaction rate. Various thermodynamic parameters have been computed and a suitable mechanism consistent with kinetic results has been proposed. The following rate law equation was deduced :

$$-\frac{d}{dt}[\text{NBS}] = \frac{2k_1k_2}{k_{-1} + k_2} [\text{PhCOMe}] [\text{H}^+]$$

Phenyl glyoxal was identified as end product of the reaction.

KINETIC investigations involving acetophenone and various oxidising agents have been reported¹⁻⁵. N-bromosuccinimide is a potent oxidising agent and has been used in the determination of several organic

of NBS left in each set was estimated. Experiments showed that one mole of acetophenone consumes two moles of NBS and therefore the following equation may be formulated:



compounds^{6,7}. Little information is available on the oxidative kinetics involving NBS. Kinetics on the oxidation of alcohols^{8,9}, esters¹⁰ and ketones¹¹⁻¹² by NBS are reported. The present paper incorporates the kinetics and mechanistic study of the oxidation of acetophenone with NBS in perchloric acid media.

EXPERIMENTAL

Pure, Rhodia, SISCO sample of acetophenone and G.R.S. Merck sample of NBS were used. Acetophenone was prepared in 50% (A.R.) methanol. NBS solution was prepared fresh and its strength was checked by iodometric method. Succinimide and mercuric acetate used were of H & W (England) and E. Merck (Germany) grade respectively. Sodium perchlorate and perchloric acid were of analaR grade. Triple distilled water was used throughout and the reaction stills blackened from outside.

All reactants except acetophenone were mixed and the reaction was initiated by adding appropriate amounts of acetophenone. The kinetics were followed by estimating unconsumed NBS iodometrically using starch indicator. Rate studies were carried out at constant temperature (± 0.1).

RESULTS AND DISCUSSION

Several sets of experiments with varying ratios of NBS over acetophenone were carried out. The excess

The end product phenyl glyoxal was identified by conventional spot test analysis¹³ and also through a DNP derivative¹⁴.

The experiments were carried out at several concentrations of NBS and acetophenone at constant hydrogen ion concentration (Table I). A zero order rate constant in NBS was observed as the rate of the reaction was found to be independent of initial NBS concentration. A proportional increase in the zero order rate constant was observed with increase in initial concentrations of acetophenone (Fig. 1). The average values of the first order rate constants calculated as $k_1' = k_0/[\text{Acetophenone}]$ were found as 4.98, 7.42 × 10⁻⁵ sec⁻¹ at 40°, 45° respectively.

A linear increase in the zero order rate constant was observed with increase in initial concentration of hydrogen ion (Fig. 2) and the zero order rate constants computed from the slopes of the plots are compiled in Table II.

The average values of first order rate constants in H⁺ calculated as $k_1' = k_0/[\text{HClO}_4]$ were found as 3.06, 4.65 × 10⁻⁶ sec⁻¹ at 40°, 45° respectively.

Sodium perchlorate, mercuric acetate and succinimide variations had negligible effect on the rate of the reaction.

Various rate parameters, viz., energy of activation (E_a), frequency factor (A), entropy of activation (ΔS[‡]),

* For correspondence.

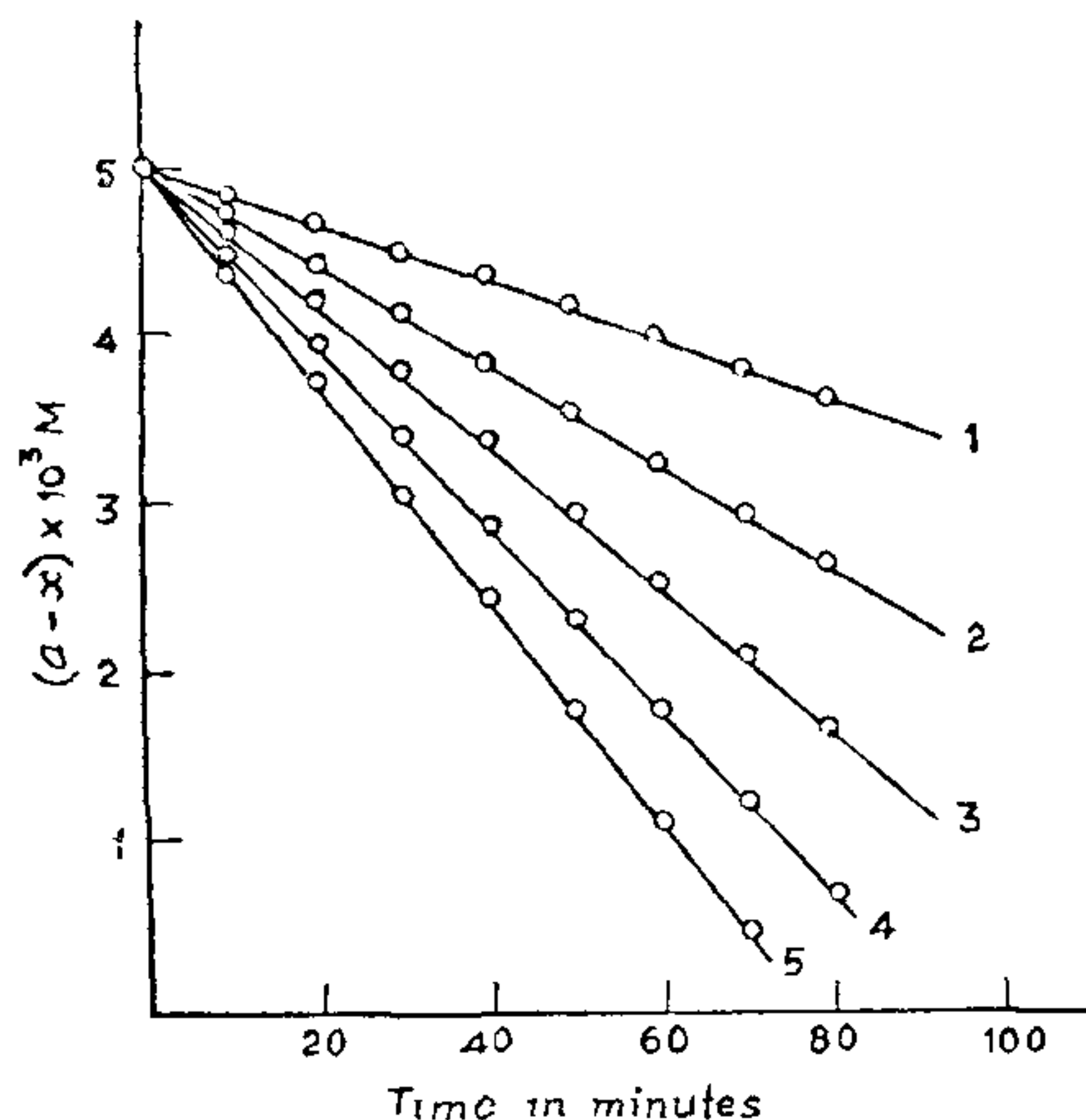


FIG. 1. Zero order rate plots at 40°, [NBS] = 1.0×10^{-3} M, $[\text{HClO}_4] = 0.16$ M, $[\text{Hg}(\text{OAc})_2] = 2.0 \times 10^{-3}$ M, [Acetophenone] = 0.6, 1.0, 1.4, 1.8 and 2.2×10^{-2} M in 1, 2, 3, 4 and 5 respectively.

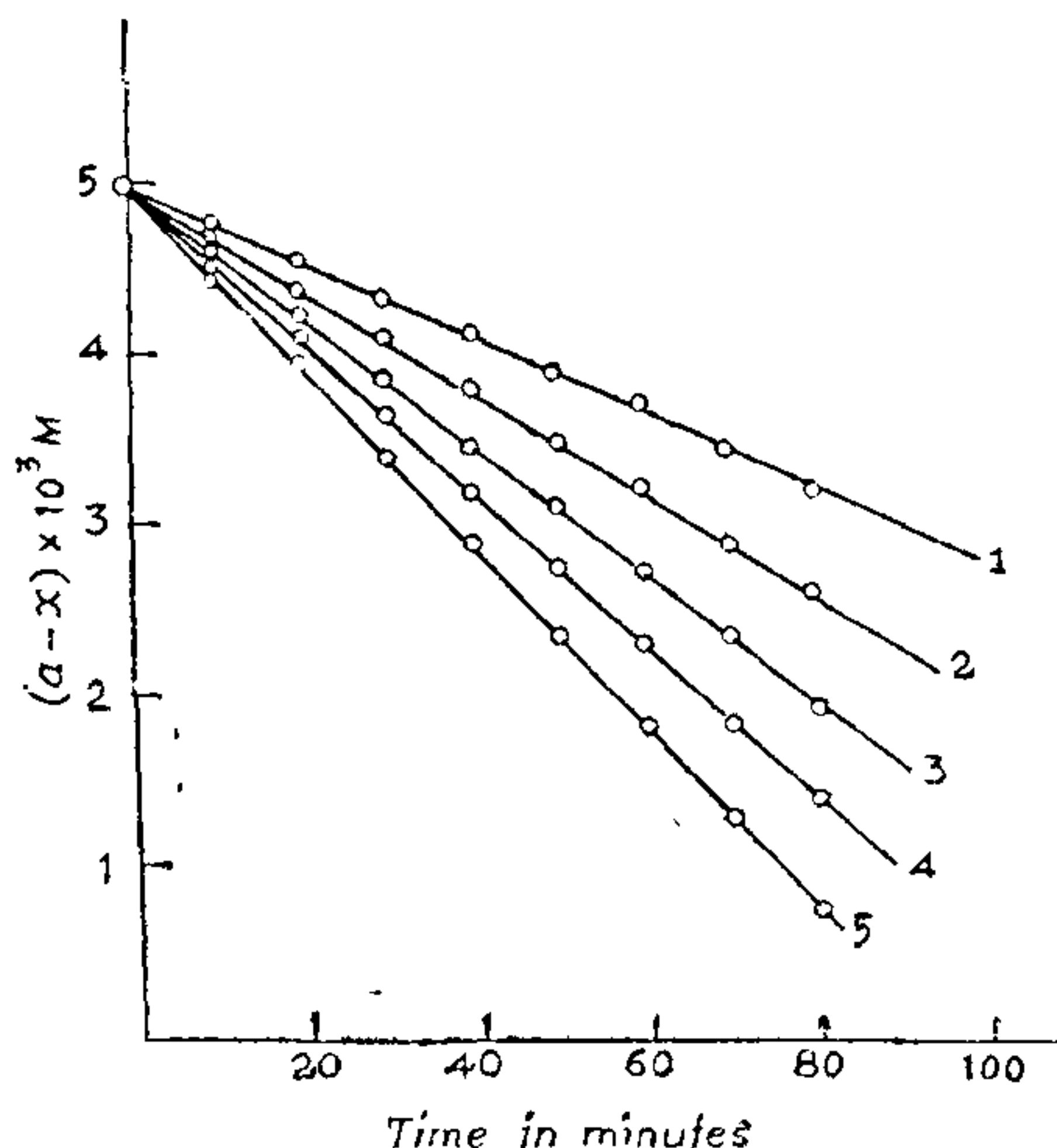


FIG. 2. Zero order rate plots at 40°. (NBS) = 1.0×10^{-3} M, [Acetophenone] = 1.0×10^{-2} M, $[\text{Hg}(\text{OAc})_2] = 2.0 \times 10^{-3}$ M, $[\text{HClO}_4] = 1.2, 1.6, 2.0, 2.4$ and 2.8×10^{-1} M in 1, 2, 3, 4 and 5 respectively.

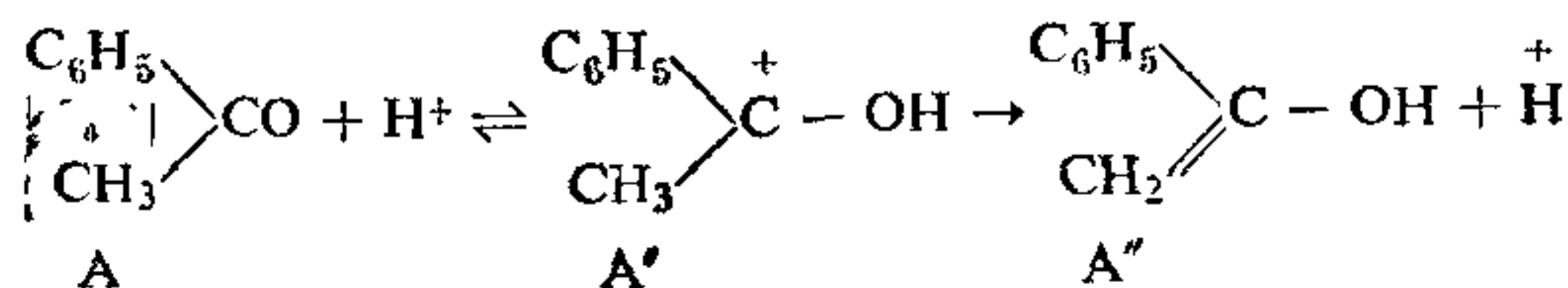


TABLE I

Effect of reactant concentration on the reaction rate, $[\text{HClO}_4] = 0.16$ M, $[\text{Hg}(\text{OAc})_2] = 2.0 \times 10^{-3}$ M

$10^3 [\text{NBS}]$ M	$10^2 [\text{Aceto-phenone}]$ M	$k_0 \times 10^7 \text{ mol. l}^{-1} \text{ sec}^{-1}$	
		40°	45°
0.8	1.0	4.67	7.33
1.0	1.0	5.00	7.50
1.2	1.0	5.17	7.17
1.4	1.0	4.83	7.67
1.6	1.0	5.25	7.83
1.0	0.6	3.00	4.33
1.0	1.4	7.00	10.33
1.0	1.8	9.08	13.33
1.0	2.2	10.83	16.67

TABLE II

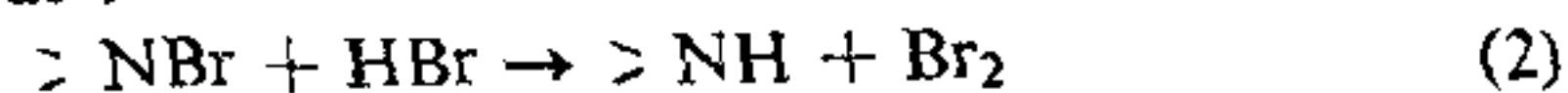
Effect of hydrogen ion concentration on the reaction rate $[\text{NBS}] = 1.0 \times 10^{-3}$ M, $[\text{Acetophenone}] = 1.0 \times 10^{-2}$ M, $[\text{Hg}(\text{OAc})_2] = 2.0 \times 10^{-3}$ M

$[\text{HClO}_4]$ M	$k_0 \times 10^7 \text{ mol. l}^{-1} \text{ sec}^{-1}$	
	40°	45°
0.12]	3.67	5.50
0.16	5.00	7.50
0.20	6.33	9.42
0.24	7.50	11.33
0.28	8.38	13.17

heat of activation (ΔH^\ddagger) and free energy of activation (ΔF^\ddagger) were computed and average values were found as $16.3 \text{ K} \cdot \text{cals} \cdot \text{mol}^{-1}$, $6.43 \times 10^7 \text{ l} \cdot \text{mol}^{-1} \cdot \text{sec}^{-1}$, -23.9 e.u. , $15.7 \text{ K} \cdot \text{cals} \cdot \text{mol}^{-1}$ and $23.3 \text{ K} \cdot \text{cals} \cdot \text{mol}^{-1}$ from the rate study measurements carried out at five temperatures (35° – 55°).

In acidic media NBS is known to exist in three different forms, viz., NBS itself, Br^+ or NBSH^+ as reported in our earlier papers.^{11,12}

It may be pointed out that all kinetic studies have been made in presence of $\text{Hg}(\text{OAc})_2$ in order to avoid any possible bromine oxidation which may be produced as :



Mercuric acetate acts as a scavenger for any Br^- formed in the reaction and exists as HgBr_4^{2-} or unionized HgBr_2 and thus ensuring pure NBS oxidation¹⁵.

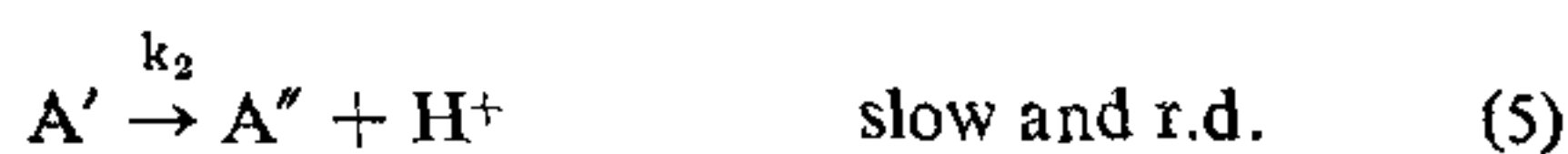
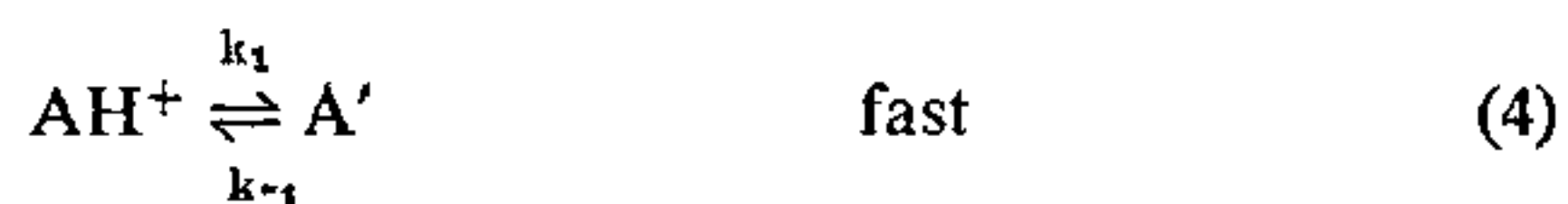
Under the experimental condition acetophenone is known to enolise as follows:

(3)

where A represents acetophenone, A' the conjugate acid and A'' its enolic form.

As the reaction is zero order with respect to NBS and from stoichiometry it has been seen that one mole of acetophenone consumes two moles of NBS, the following mechanistic scheme with NBS as the oxidising species is postulated, taking into account Littler and Waters contention¹⁶, that in the case of two electron abstracting oxidation processes, enolisation will be the slow and rate determining step.

NBS as oxidising species



Intermediate species



Application of steady state treatment to A', A'' and X gives equations (8), (9) and (10) respectively as follows:

$$k_1 [\text{A}] [\text{H}^+] = k_{-1} [\text{A}'] + k_2 [\text{A}'] \quad (8)$$

$$k_2 [\text{A}'] = k_3 [\text{A}''] [\text{NBS}] \quad (9)$$

$$k_3 [\text{A}''] [\text{NBS}] = k_4 [\text{X}] [\text{NBS}] \quad (10)$$

Now the rate of disappearance of NBS is given by:

$$-\frac{d}{dt} [\text{NBS}] = k_3 [\text{A}''] [\text{NBS}] + k_4 [\text{X}] [\text{NBS}] \quad (11)$$

From equations (9), (10) and (11) we have

$$-\frac{d}{dt} [\text{NBS}] = 2k_2 [\text{A}'] \quad (12)$$

Substituting the values of [A'] from equation (8) in equation (12), we get the rate law as follows:

$$-\frac{d}{dt} [\text{NBS}] = \frac{2k_1 k_2}{k_{-1} + k_2} [\text{A}] [\text{H}^+] \quad (13)$$

which is in complete accord with the kinetic parameters.

Further it can be shown that the possibility that Br⁺ or NBSH⁺ acting as the alternative oxidising species, may be ruled out on the basis that the mechanistic models postulated in such cases may involve steps which may be highly conjectural in nature.

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