

Oxidation of Aliphatic Ketone Semicarbazones by Acid Bromate: A Kinetic and Mechanistic Study

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Kinetics of oxidation of semicarbazones by acid bromate in 25% aqueous acetic acid medium in the presence of perchloric acid has been investigated. The rate has first order dependence in [oxidant], fractional order in [substrate] and inverse fractional order in $[H_3O^+]$. Addition of the reaction product, potassium bromide and variation of ionic strength of the medium have no effect on the rate. The rate increases with decrease in dielectric constant of the medium. Activation parameters have been evaluated from the Eyring plots. The stoichiometric studies reveal that the reactants react in 1 : 1 mole ratio *via* the formation of a complex. Mechanism consistent with the observed kinetics has been proposed and the related rate law derived.

Key Words: Kinetic, Mechanistic, Acid bromate, Oxidation, Alkanone semicarbazones.

INTRODUCTION

Potassium bromate has been widely used as an effective oxidant for a wide variety of organic substrates¹⁻³. The kinetics of oxidation of ketones, gallic acid, thiosemicarbazide, anisole, etc., by potassium bromate in aqueous acetic acid medium in the presence of perchloric acid have been reported. But no information is available on the oxidation of aliphatic ketone semicarbazones by acid bromate in aqueous acidic media. We herein report the results of investigations on the oxidation of aliphatic ketone semicarbazones by acid bromate in the presence of perchloric acid in aqueous acetic acid medium.

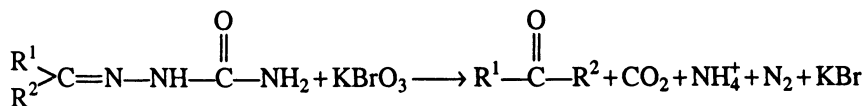
EXPERIMENTAL

Analytical grade [EQ. Qualigens] potassium bromate, semicarbazide hydrochloride, sodium acetate trihydrate, perchloric acid, sodium perchlorate were used. All other reagents used were of excellent grade. The samples of propanone semicarbazone (1), butanone semicarbazone (2), 3-pentanone semicarbazone (3) were prepared by reacting requisite amounts of respective ketones, semicarbazide hydrochloride and sodium acetate. The kinetic measurements were initiated by

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the rapid addition of appropriate volumes of oxidant solution, thermally equilibrated at a desired temperature, to a mixture containing known amounts of substrate in acetic acid-water mixture in presence of HClO_4 pre-equilibrated at the same temperature. The progress of the reaction was monitored by iodometric estimation of unreacted oxidant at regular intervals of time.

The stoichiometric results indicate that 1 mol of the substrate required 1 mol of the oxidant as represented by the following empirical equation:



The products of the oxidation reaction were identified by the usual tests.

RESULTS AND DISCUSSION

The oxidation of aliphatic ketone semicarbazones follows first-order kinetics with respect to $[\text{Oxidant}]_T$ when the $[\text{Substrate}]$ is kept in large excess (more than 10-fold) over that of $[\text{Oxidant}]$. This is evidenced by the linear plots of $\log (\text{KBrO}_3)_T$ vs. time (Fig. 1, Table-1).

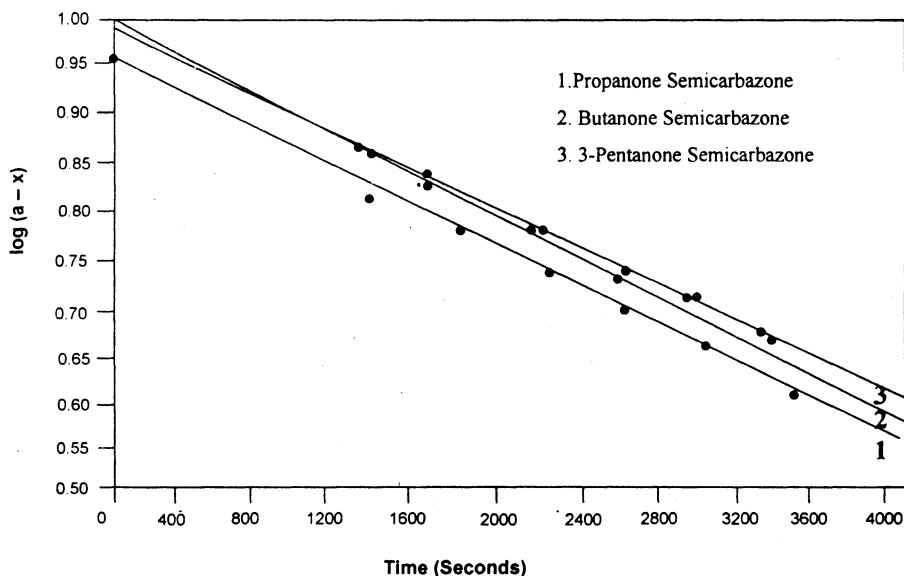


Fig. 1. Dependence of rate on the concentration of KBrO_3 : plot of $\log (a - x)$ vs. time

The rate increased linearly with $[\text{substrate}]$ and the plot of $\log k_1$ vs. $\log [\text{substrate}]$ is a straight line with slope less than unity indicating the fractional order dependence of the reaction on $[\text{substrate}]$. Rate constant values decrease linearly with increase in $[\text{H}_3\text{O}^+]$. The plot of $\log (1/k)$ vs. $\log [\text{H}_3\text{O}^+]$ is a straight line with fractional slope indicating the order with respect to $[\text{H}_3\text{O}^+]$ is fractional. The rate increases marginally with decrease in dielectric constant of the medium

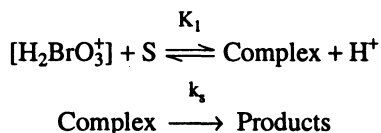
effected by increasing the percentage of acetic acid. This fact is supported by the fact that the plot of k_1 vs. $1/D$ is a curve (Table-1). Variation of ionic strength of the medium has negligible effect on the rate of the reaction, whereas the added potassium bromide has no effect on the rate of the reaction in the concentration range (2.016×10^{-4} M to 8.066×10^{-4} M). Polymerization with added acrylamide is not observed, eliminating free radical pathway. The values of various thermodynamic parameters have been evaluated from the measurements of rates of the reactions at various temperatures between 293 K–308 K for all the substrates.

TABLE-1
FIRST ORDER RATE CONSTANTS (k_{obs}) FOR OXIDATION OF
ACETONE SEMICARBAZONE (1) BY ACID BROMATE IN
AQUO-ACETIC ACID MEDIUM IN PRESENCE
OF PERCHLORIC ACID AT 293 K

10^3 [Oxidant] (mol dm ⁻³)	10^2 [Substrate] (mol dm ⁻³)	[HClO ₄] (mol dm ⁻³)	% AcOH (v/v)	10^4 (k_{obs} s ⁻¹)
1.197	5.211	1.0	25	2.223
1.497	5.221	1.0	25	2.252
1.796	5.211	1.0	25	2.664
1.497	3.908	1.0	25	1.919
1.497	6.514	1.0	25	2.539
1.497	7.817	1.0	25	2.778
1.497	9.119	1.0	25	3.015
1.497	5.211	1.0	30	2.489
1.497	5.211	1.0	35	2.558
1.497	5.211	1.0	40	2.623

In acid bromate solutions BrO_3^- , HBrO_3^+ , BrO_3^+ , etc. are reported as possible reactive species⁹. On the basis of the observed results in the present study, $[\text{H}_2\text{BrO}_3^+]$ is proposed as the actual reacting species.

Mechanism



where 'S' is substrate.

Scheme-1

A mechanism involving the deprotonation of H_2BrO_3^+ when it attacks the substrate to form a complex in a pre-equilibrium step is invoked to account for the inverse dependence of the titled reaction of $[\text{H}_3\text{O}^+]$. Based on Scheme-1, the following rate law has been derived:

$$\frac{1}{K_{\text{obs}}} = \frac{[\text{H}^+]}{k_s K_1} \frac{1}{[\text{S}]} + \frac{1}{k_s}$$

TABLE-2
DEPENDENCE OF RATE ON THE CONCENTRATION OF
PERCHLORIC ACID AND SODIUM PERCHLORATE

10^3 [Oxidant] (mol dm ⁻³)	10^2 [Substrate] (mol dm ⁻³)	[HClO ₄] (mol dm ⁻³)	[NaClO ₄] (mol dm ⁻³)	(%) AcOH (v/v)	10^4 (k_{obs} s ⁻¹)
1.497	5.211	0.80	0.35	25	2.878
1.497	5.221	0.90	0.25	25	2.610
1.796	5.211	0.95	0.20	25	2.505
1.497	5.211	1.00	0.15	25	2.372
1.497	5.211	1.10	0.05	25	2.175
1.497	5.211	1.00	0.05	25	2.424
1.497	5.211	1.00	0.10	25	3.348
1.497	5.211	1.00	0.15	25	2.372
1.497	5.211	1.00	0.20	25	2.412
1.497	5.211	1.00	0.25	25	2.377

TABLE-3
RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE
OXIDATION OF ALIPHATIC KETONE SEMICARBAZONES
BY ACID BROMATE

Substituent		10^4 (k (s ⁻¹))				ΔH^* (kJ mol ⁻¹)	ΔS^* (J mol ⁻¹ K ⁻¹)	ΔG^* (kJ mol ⁻¹)
R ¹	R ²	293 K	298 K	303 K	308 K			
CH ₃	CH ₃	2.252	2.797	3.363	4.009	23.16	-100.11	52.49
CH ₃	CH ₂ CH ₃	2.512	3.027	3.710	4.350	24.33	-96.86	52.70
CH ₂ CH ₃	CH ₂ CH ₃	2.722	3.224	3.915	4.606	23.51	-98.01	52.22

The observed order of reactivity among the semicarbazones studied is propanone semicarbazone (1) < butanone semicarbazone (2) < 3-pentanone semicarbazone (3). This trend in reactivity of these substrates can be understood from the fact that as the size of the alkyl group increases its electron donating ability increases. The fairly constant values of ΔH^* lend support to the fact that similar mechanism operates in each of these cases. The observed negative entropy of activation indicates that the transition state of the rate determining step is more ordered than the initial stage.

The double-reciprocal plot of k_1^{-1} vs. [substrate]⁻¹ is linear with positive intercept on the rate axis confirming the intermediate formation of the complex during the course of the reaction.

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