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A Comparative Study of Kinetics of HCl and $HClO_4$ Acid Catalyzed Oxidation of 2-Butanone by Selenium Dioxide in Aqueous Acetic Acid Medium

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Hydrochloric and perchloric acid catayzed oxidation of 2-butanone by selenium dioxide has been studied in 70% aqueous acetic acid medium. The reactions show first order dependence in oxidant $[SeO_2]$. The order of reaction with respect to substrate, hydrochloric acid and perchloric acid is one. Effect of dielectric constant of medium and effect of neutral salt has also been investigated. Various thermodynamic parameters have also been evaluated. End products have been identified as 2,3-diketone. A probable mechanism has been suggested on the basis of experimental results of both acids.

Key words: Kinetics, Selenium dioxide, 2-Butanone, Oxidation.

INTRODUCTION

Selenium dioxide has been used as an oxidant, in absence and presence of mineral acids, for the oxidation of various organic substrates such as aldehydes[1], alcohols[1], esters[2], olefins[4], desoxybenzoin[5], acetylacetone[6] and 2-alkanones[7,8], ketones[1,3,9], etc. In the literature the hydrochloric acid catalyzed oxidation of 2-butanone by selenium dioxide has not yet been reported. The presence of H^+ is known to accelerate the oxidation of organic substrates The strength of $HClO_4$ is more than HCl in acetic acid and aqueous acetic acid[10]. In spite of this the experimental findings pertaining to oxidation of 2-butanone by selenium dioxide have revealed that HCl catalyzed oxidation is about three times faster than of $HClO_4$. This result prompted us to undertake the comparative study of kinetics of HCl and $HClO_4$ catalyzed oxidation of 2-butanone by the aforesaid oxidant, with a view to know the difference between them.

EXPERIMENTAL

2-Butanone (SISCO), selenium dioxide (Loba); HCl, $HClO_4$ and acetic acid (AnalaR); NaCl and $NaClO_4$ (CDH) were used. Stock solution of oxidant was prepared in distilled water and standardized iodometrically. Solution of 2-butanone was prepared in glacial acetic acid. Required solutions of HCl and $HClO_4$

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were prepared by dilution of stock solutions up to required concentration. Reaction was initiated by mixing the solutions of 2-butanone in acetic acid and selenium dioxide in presence of HCl or $HClO_4$ (both solutions were pre-equilibrated at the reaction temperature). The reaction was followed by estimating the unreacted selenium dioxide iodometically under pseudo first order conditions $[SeO_2] \ll$ [2-Butanone] and [acid][11]. The end product was identified[12] by spot test as 2,3-diketone.

The stoichiometric results show that approximately one mole of selenium dioxide is required for the complete oxidation of one mole of 2-butanone.

$$SeO_2 + CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_3 \longrightarrow CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-CH_3 + SeO_2 + H_2O$$

2,3-diketone

The test for free radical was found negative while the presence of free selenium was identified qualitatively[13].

RESULTS AND DISCUSSION

The results of oxidation of 2-butanone studied by varying concentration of selenium dioxide (Table-1, Fig. 1 a, b) show that order of reaction with respect to oxidant is unity.

TABLE-1
EFFECT OF SELENIUM DIOXIDE CONCENTRATION
[2-Butanone] = 5×10^{-1} M, Temp. = 313 K, [Acid] = 1×10^{-1} M, $HOAc-H_2O$ = 70% (v/v)

$[SeO_2] \times 10^3$ M	2.5	5.0	7.5	10.0	12.5
$k_1 \times 10^5$ S^{-1} (a)	21.37	19.31	18.35	17.52	16.38
$k_1 \times 10^5$ S^{-1} (b)	7.35	5.29	4.97	4.77	4.58

(a) = HCl, (b) = $HClO_4$

Variation in 2-butanone concentration (Table-2, Fig.-2), shows pseudo first order dependence on susbstrate.

TABLE-2
EFFECT OF 2-BUTANONE CONCENTRATION
$[SeO_2] = 1 \times 10^{-2}$ M Temp. = 313 K, [Acid] = 1×10^{-1} M, $HOAc-H_2O$ = 70% (v/v)

[2-Butanone] $\times 10^{-1}$ M	4	5	6	7	8
$k_1 \times 10^5$ S^{-1} (a)	3.75	17.52	21.48	24.84	28.57
$k_1 \times 10^5$ S^{-1} (b)	3.83	4.77	5.73	6.69	7.64

(a) = HCl, (b) = $HClO_4$

Oxidation of 2-butanone by selenium dioxide in different concentrations of HCl and $HClO_4$ (Table-3) shows the first order dependence in concentration of acids.

TABLE-3
EFFECT OF ACID CONCENTRATION [2-Butanone] = 5×10^{-1} M
$[SeO_2] = 1 \times 10^{-2}$ M, Temp. = 313 K, HOAc—H_2O = 70% (v/v)

$[HCl] \times 10^2$ M	5	10	15	20	25
$k_1 \times 10^5\ S^{-1}$	8.89	17.52	27.34	35.69	44.70
$[HClO_4] \times 10^2$ M	5	10	15	20	25
$k_1 \times 10^5\ S^{-1}$	2.37	4.77	7.16	9.56	11.96

Addition of salts like NaCl and $NaClO_4$ in HCl and also in $HClO_4$ catalyzed reactions shows nominal accelerating effect on rate of reaction (Table-4), indicating the rate determining step involves a neutral molecule[14].

TABLE-4
EFFECT OF NEUTRAL SALT [2-Butanone] = 5×10^{-1} M
$[SeO_2] = 1 \times 10^{-2}$ M, Temp. = 313 K, [Acid] = 1×10^{-1} M, HOAc-H_2O = 70% (v/v)

$[NaCl] \times 10^3$ M	0.0	2.5	5.0	7.5	10.0
$k_1 \times 10^5\ S^{-1}$ (a)	17.50	17.66	17.82	17.94	18.04
$[NaClO_4] \times 10^3$ M	0.0	2.5	5.0	7.5	10.0
$k_1 \times 10^5\ S^{-1}$ (b)	4.77	4.86	4.93	4.98	5.09

(a) = HCl, (b) = $HClO_4$

The rate of reaction increases when dielectric constant of medium decreases in case of $HClO_4$ catalyzed oxidation of 2-butanone by selenium dioxide. The plot of log k *vs.* 1/D is linear with positive slope. This suggests that the reaction is probably of positive-ion dipole type[15]. A plot of log k *vs.* (D – 1) (2D + 1) is linear in case of HCl catalyzed oxidation of 2-butanone by selenium dioxide, suggesting the reaction to be of dipole-dipole type (Table-5).

TABLE-5
EFFECT OF PERCENTAGE OF ACETIC ACID ON REACTION RATE
[2-Butanone] = 5×10^{-1} M, $[SeO_2] = 1 \times 10^{-2}$ M, [Acid] = 1×10^{-1} M, Temp. = 313 K.

[HOAc-H_2O]% (v/v)	60	65	70	75	80
$k_1 \times 10^5\ S^{-1}$ (a)	8.88	12.40	17.50	27.39	53.45
$k_1 \times 10^5\ S^{-1}$ (b)	1.40	2.50	4.77	11.26	28.30

(a) = HCl, (b) = $HClO_4$

Various thermodynamic parameters have been evaluated and the results are tabulated in Table-6.

TABLE-6
THERMODYNAMIC PARAMETERS

	E_a (KJ mol^{-1})	A (sec^{-1})	$\Delta H^{\#}$ (KJ mol^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (J K^{-1} mol^{-1})
HCl catalyzed	57.21	5.64×10^6	54.58	97.43	–136.89
$HClO_4$ catalyzed	55.97	2.28×10^8	53.29	100.81	–151.81

Mechanism and rate expression: From Table-1 it is evident that HCl catalyzed oxiation of 2-butanone by selenium dioxide is much more pronounced than of $HClO_4$, under identical conditions. The literature suggests that probably more reactive species of SeO_2 is being generated in the reaction mixture of HCl catalyzed oxidation[9].

$$SeO_2 + H_2O \longrightarrow H_2SeO_3$$

$$H_2SeO_3 + HCl \longrightarrow HO\text{—}\underset{\underset{\displaystyle O}{\|}}{Se}\text{—}Cl + H_2O$$

whereas $H_3SeO_3^+$ and $AcH_2SeO_3^+$ species may be the probable active oxidizing species of SeO_2 in the reaction mixture of $HClO_4$ catalyzed oxidation of 2-butanone[7, 9].

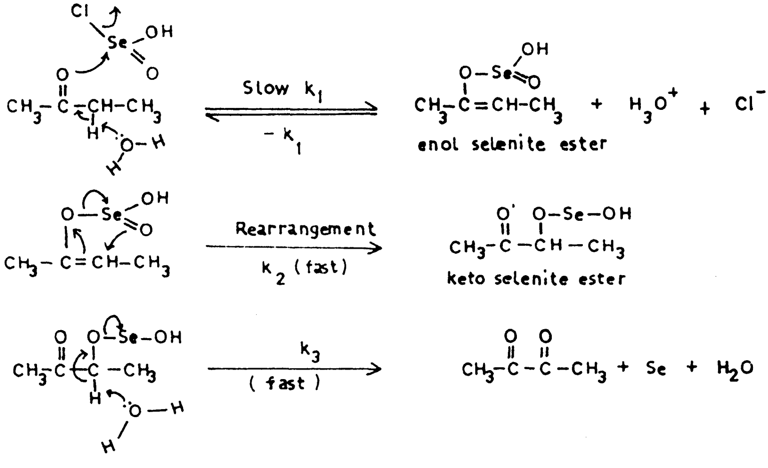
$$SeO_2 + H_2O \longrightarrow H_2SeO_3$$

$$H_2SeO_3 + HOAc \longrightarrow AcHSeO_3 + H_2O$$

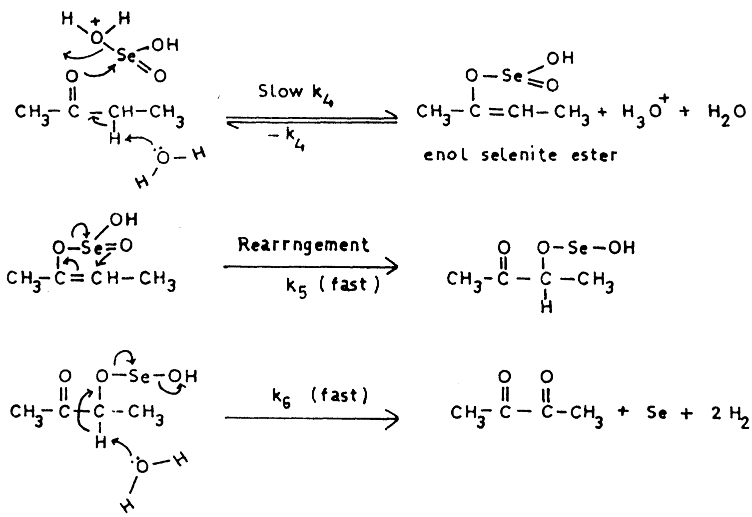
$$AcHSeO_3 \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} AcH_2SeO_3^+$$

$$H_2SeO_3 \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} H_2SeO_3^+$$

In the above oxidizing species, $HO\text{—}\underset{\underset{\displaystyle O}{\|}}{Se}\text{—}Cl$ and $AcH_2SeO_3^+$ (or $H_3SeO_3^+$), the chloride is better leaving group than H_3O^+, so that the enhanced formation of enol selenite ester may be responsible for the pronounced rate of reaction in case of HCl **(Scheme-A)** than in $HClO_4$ catalyzed oxidation **(Scheme-B).**



(Scheme-A)



(Scheme-B)

Rate Law Derivation: From first step rate of disappearance of oxidizing species of SeO_2,

$$\frac{-d[\text{Oxidant}]}{dt} = k_1[\text{substrate}][\text{oxidant}] - k_{-1}[\text{enol selenite ester}]$$

Rate of formation of product is given by:

$$\frac{-d[\text{product}]}{dt} = k_{-1}[\text{enol selenite ester}]$$

Rate of formation of enol selenite ester is given by:

$$\frac{d}{dt}[\text{enol selenite ester}] = k_1[\text{substrate}][\text{oxidant}] - k_{-1}[\text{enol selenite ester}][H_3O^+][X]$$

$$- k_2 [\text{enol slenite ester}]$$

where [X] = [Cl] or $[H_2O]$.

But in overall reaction, $\frac{d}{dt}[\text{enol selenite ester}] = 0$.

Thus $$\frac{d}{dt}[\text{enol selenite ester}] = \frac{k_1[\text{substrate}][\text{oxidant}]}{k_{-1}[H_3O^+][X] + k_2}$$

$$\frac{d[\text{oxidant}]}{dt} = \frac{d[\text{product}]}{dt} = k_2\frac{k_1[\text{substrate}][\text{oxidant}]}{k_{-1}[H_3O^+][X] + k_2}$$

But as $k_2 >> k_1$,

$$\frac{d}{dt}[\text{oxidant}] = \frac{k_2k_1[\text{substrate}][\text{oxidant}]}{k_2}$$

$$\frac{d}{dt}[\text{oxidant}] = k_1[\text{substrate}][\text{oxidant}]$$

(a) When oxidation is catalyzed by HCl,

$$[\text{oxidant}] \propto [H_2SeO_3][HCl]$$

$$\frac{d}{dt}[\text{oxidant}] = k_1k[\text{substrate}][H_2SeO_3][HCl]$$

(a) When oxidation is catalyzed by $HClO_4$,

$$[\text{oxidant}] \propto [H_2SeO_3]\,[H^+]$$

$$\frac{d}{dt}[\text{oxidant}] = k_4k'[\text{substrate}][H_2SeO_3][H^+]$$

Thus the derived rate laws explain the observed kinetics of HCl and $HClO_4$-catalysed oxidation of 2-butanone by selenium dioxide.

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