

Applicability of Hammett Equation to Insulated Systems— Kinetics of Oxidation of Substituted Phenoxyacetic Acids by Ce(IV)

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The kinetics of oxidation of substituted phenoxyacetic acids by ceric ammonium nitrate (CAN) in perchloric acid has been studied spectrophotometrically in aqueous acetic acid. The order with respect to Ce(IV) is one and the order with respect to phenoxyacetic acid is found to be 0.5. A plot of k_{obs}^{-1} versus $[\text{substrate}]^{-1}$ is linear with an intercept on the rate axis suggests the formation of an equilibrium complex between the reactants prior to the rate determining step.

INTRODUCTION

Kinetics of Ce(IV) oxidation of several organic substrates are well documented¹⁻⁸. But the use of insulated acid substrate in a similar study is rare. The kinetics of oxidation of phenoxyacetic acid with acid permanganate⁹ and N-chloropiperidone¹⁰ have already been reported.

In continuation of our investigation¹¹⁻¹⁴ into the reactions involving insulated systems, we now report in this paper the kinetics and mechanism of oxidation of substituted phenoxyacetic acids by Ce(IV) in aqueous acetic acid.

EXPERIMENTAL

Materials and Methods

Phenoxyacetic acids were prepared by the method of Koelsch¹⁵, ceric ammonium nitrate (E. Merck) was used as such. Acetic acid was purified by the method of Weissberger¹⁶. All the other chemicals used were of AR grade.

The stock solutions of phenoxyacetic acids and ceric ammonium nitrate were prepared in acetic acid (50% (v/v)). Ceric ammonium nitrate was standardised using standard ferrous sulphate.

The kinetics was followed spectrophotometrically in JASCO-340 spectrometer at 340 nm. The change in the oxidant (ceric ammonium nitrate) concentration with time was directly measured. In all the kinetic measurements pseudo first order condition was maintained. All the rate constants were reproducible within $\pm 3\%$. The pseudo first order rate constant k_{obs} was obtained from $\log [\text{oxidant}]$ versus time plot by the method of least squares.

Stoichiometry and Product Analysis

Equal moles of substrate and oxidant were mixed and kept at room temperature for 2 days under kinetic conditions. Then the mixture was extracted by ether and purified. The product benzoquinone was identified by IR spectrum and TLC.

Thus under the given kinetic conditions stoichiometry of the reaction was found to be 1 : 1.

RESULTS AND DISCUSSION

Effect of Oxidant

The oxidation of the acid follows a first order dependence with respect to Ce(IV) over a range of concentration $2.3-18.2 \times 10^{-4}$ M, as evidenced by the linearity of plot, $\log [\text{oxidant}]$ versus time (Table 1).

TABLE 1
EFFECT OF VARYING SUBSTRATE AND OXIDANT ON REACTION RATE
[HOAc] = 50% (v/v); [HClO₄] × 10 = 1.028 mol dm⁻³; Temp. = 35°

10 ³ [Substrate] (mol dm ⁻³)	10 ⁴ [Oxidant] (mol dm ⁻³)	10 ³ × <i>k</i> _{obs} (sec ⁻¹)	10 ² × <i>k</i> _{1.5} dm ^{1.5} mol ^{-0.5} sec ⁻¹)
2.00	2.30	1.43	—
2.00	9.10	1.42	—
2.00	13.60	1.45	—
2.00	18.20	1.41	—
0.90	8.84	0.86	9.06
1.60	8.84	1.13	8.93
2.30	8.84	1.32	8.70
3.20	8.84	1.62	9.06

Effect of Substrate

At constant [H⁺], [Oxidant] and temperature $\log k_{\text{obs}}^{-1}$ versus $\log [\text{substrate}]^{-1}$ is also linear and the slope is 0.5 ($r = 0.992$; $Sd = 0.025$; $n = 4$). Hence the order with respect to substrate is 0.5.

The plot of k_{obs}^{-1} versus $[\text{substrate}]^{-1}$ is linear making intercept on the rate axis pointing to the formation of an equilibrium complex between Ce(IV) species and substrate. The k_{obs} and $k_{1.5}$ are given in Table 1.

Effect of Perchloric Acid

The reaction is considerably influenced by the variation in the acidity of the medium at constant ionic strength over a range of perchloric acid concentration, $0.51-2.57 \times 10^{-1}$ M (Table 2). A plot (not shown) of k_{obs}^{-1} versus $[\text{H}^+]^{-1}$ is in agreement with the general observation, that increase

of $[H^+]$ increases the concentration of the effective oxidant⁸, viz., unhydrolysed Ce(IV) aq.

TABLE 2
EFFECT OF VARYING PERCHLORIC ACID
CONCENTRATION ON THE REACTION RATE

$[Oxidant] \times 10^4 = 8.84 \text{ mol dm}^{-3}$; $[Substrate] \times 10^2 = 1.00 \text{ mol dm}^{-3}$;
 $[HOAc] = 50\% (v/v)$; Temp. = 35°

$10 [HClO_4]$ (mol dm^{-3})	$10^3 \times k_{obs}$ (sec^{-1})
0.51	0.64
1.03	1.46
1.54	2.31
2.06	3.25
2.57	4.08

Effect of Acrylonitrile

The clear reaction mixture containing phenoxyacetic acid and cerium ammonium nitrate when allowed to stand with a drop of acrylonitrile became turbid and within a few minutes the entire mixture turned viscous, showing that the oxidation process involves a free radical mechanism.

Effect of Ionic Strength

With the increase of ionic strength at constant $[H^+]$, $[substrate]$ and $[oxidant]$, the k_{obs} also increases indicating that the oxidation reaction involves an ion-molecule interaction. The rate constants determined with various amounts of added perchlorate (0.99 – $2.99 \times 10 \text{ M}$) are given in Table 3.

TABLE 3
EFFECT OF IONIC STRENGTH ON THE REACTION RATE
 $[Oxidant] \times 10^4 = 8.84 \text{ mol dm}^{-3}$; $[Substrate] \times 10^2 = 1.00 \text{ mol dm}^{-3}$;
 $[HClO_4] \times 10^2 = 10.3 \text{ mol dm}^{-3}$; $[HOAc] = 50\% (v/v)$; Temp. = 35°

$10[NaClO_4]$ (mol dm^{-3})	$10^3 \times k_{obs}$ (sec^{-1})
0.99	1.09
1.50	1.34
1.99	1.42
2.49	1.49
2.99	1.62

Effect of Solvent

An increase in the percentage of acetic acid in the medium at constant $[H^+]$, [substrate] and [oxidant] considerably increases the reaction rate. This is due to the increase of the unhydrolysed Ce (IV) aq. which is the effective oxidising species in this reaction. The k_{obs} values are given in Table 4.

TABLE 4

EFFECT OF SOLVENT ON THE REACTION RATE
 [Oxidant] $\times 10^3 = 8.84 \text{ mol dm}^{-3}$; [Substrate] $\times 10^2 = 1.00 \text{ mol dm}^{-3}$;
 $[HClO_4] \times 10^2 = 10.3 \text{ mol dm}^{-3}$; [HOAc] = 50% (v/v); Temp. = 35°

% HOAc	$10^2 \times k_{obs}$ (sec ⁻¹)
30	0.92
40	1.08
50	1.10
60	1.37
70	1.50

Effect of Temperature

The rate constants were measured at 30°C, 35°C, 40°C and 45°C (Table 5). From the Eyrings plot the kinetic parameters are calculated. The activation parameters at 35°C are

$$E_a = 54.16 \text{ KJ mol}^{-1}; \Delta H^{\ddagger} = 52.16 \text{ KJ mol}^{-1};$$

$$-\Delta S^{\ddagger} = 107.21 \text{ JK}^{-1} \text{ mol}^{-1}; \Delta G^{\ddagger} = 85.18 \text{ KJ mol}^{-1}$$

TABLE 5

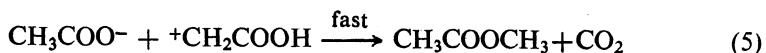
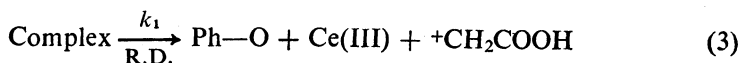
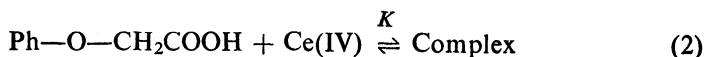
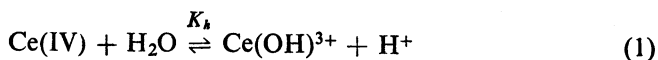
EFFECT OF TEMPERATURE ON REACTION RATE
 [Oxidant] $\times 10^4 = 8.84 \text{ mol dm}^{-3}$; [Substrate] $\times 10^2 = 1.00 \text{ mol dm}^{-3}$;
 $[HClO_4] \times 10^2 = 12.00 \text{ mol dm}^{-3}$; [HOAc] = 50% (v/v)

Temperature (°C)	$k_{obs} \times 10^3$ (sec ⁻¹)	$k_{1.5} \times 10^3$ (dm ^{1.5} mol ^{-0.5} sec ⁻¹)
30	1.61	1.60
35	2.42	2.40
40	3.21	3.20
45	4.70	4.70

Mechanism

Based on the observations recorded above the probable mechanism of

oxidation of phenoxyacetic acid by Ce(IV) is shown as:



One may presume the possibility of the formation of diphenyl peroxide as the end product, i.e., the dimer of phenoxy radical (Step 4 of the proposed mechanism). Though Walling¹⁷ reports detectable small amounts of diphenyl peroxide at -78°C , it is highly dissuaded under the experimental conditions of the present work. This is evident as the phenoxy radicals apparently having high resonance energy make the dissociation energy of the O—O bond of diphenyl peroxide so low, that it undergoes decomposition easily.

Since steps (4) and (5) can be neglected under kinetic conditions, the rate of the reaction is given by the following rate law:

$$\begin{aligned} -\frac{d[\text{Ce(IV)}]}{dt} &= \frac{k_1[\text{Ce(IV)}]_{\text{total}}}{\frac{1}{K[\text{S}]} + \frac{K_h[\text{H}_2\text{O}]}{K[\text{S}][\text{H}^+]} + 1} \\ k_{\text{obs}} &= \frac{k_1}{\frac{1}{K[\text{S}]} + \frac{K_h[\text{H}_2\text{O}]}{K[\text{S}][\text{H}^+]} + 1} \\ \frac{1}{k_{\text{obs}}} &= \frac{1}{k_1} + \frac{K_h[\text{H}_2\text{O}]}{K[\text{S}][\text{H}^+]} + \frac{1}{k_1 K[\text{S}]} \end{aligned}$$

Substituent Effects on the Reaction Rate

The kinetics was carried out with a few meta- and para-substituted phenoxyacetic acids at 30°C , 35°C and 40°C . The rate constant ($k_{1,s}$) in each case was obtained by dividing the pseudo first order rate constant by the square root of the concentration of the respective phenoxyacetic acid. The calculated rate constants ($k_{1,s}$) and the activation parameters for the oxidation of various substituted phenoxyacetic acids are given in Table 6.

From the activation parameters we know that the entropy of activation is not constant throughout the series. More generally, if the Hammett equation is valid at one temperature, the condition for its validity at any other temperature is a linear relationship between enthalpies and entropies. A plot of ΔH^{\ddagger} against ΔS^{\ddagger} gave a straight line with a correlation

TABLE 6
EFFECT OF SUBSTITUENTS ON THE REACTION RATE

Substituent	$k_{1.5} \times 10^3$ ($\text{dm}^{1.5} \text{mol}^{-0.5} \text{sec}^{-1}$)			ΔH^{**} (KJ mol^{-1})	$-\Delta S^{**}$ ($\text{JK}^{-1} \text{mol}^{-1}$)	r	S
	30°C	35°C	40°C				
None	16.00	24.00	32.11	52.16	107.21	0.996	0.044
p-OCH ₃	52.80	83.10	107.30	53.45	92.95	0.988	0.076
p-CH ₃	32.81	51.30	67.21	53.86	95.61	0.989	0.069
p-NO ₂	1.21	2.11	3.23	74.94	53.54	0.998	0.047
p-Cl	6.00	9.92	13.60	62.07	82.65	0.992	0.069
p-Br	5.90	9.60	11.61	50.89	119.51	0.969	0.117
p-I	3.20	6.03	8.43	73.95	48.49	0.985	0.115
m-OCH ₃	9.28	14.49	21.00	61.84	79.90	0.999	0.025
m-CH ₃	20.40	31.62	41.92	54.28	98.21	0.992	0.058
m-Cl	3.64	5.55	8.01	59.64	94.98	0.999	0.018

r = correlation coefficient; S = Standard deviation

coefficient, 0.960. The isokinetic temperature obtained from the slope is 376 K. If this linearity between enthalpies and entropies is true, it should predict a meaningful correlation between $\log k_{1.5}$ and σ .

Since ΔH^{**} and ΔS^{**} values are mutually dependent, the experimental data is treated by Exner's analysis. The excellent correlation ($r = 0.998$) between $(k_{1.5})_{45^\circ\text{C}}$ and $\log (k_{1.5})_{35^\circ\text{C}}$ shows that a common mechanism is followed by all the substituted acids studied.

A plot of $\log k_{1.5}$ data of the substituted acids with σ -constants gave a ρ value of -1.62 , ($r = 0.987$) showing that the applicability of Hammett equation to the present reaction is 'good'. The negative ρ value indicates that the oxygen atom of the phenoxyacetic acid is more positively charged in the transition state of the rate-determining step than in the reactant, and this is consistent with the step (3) of the mechanism proposed.

Methyl group shows a slight increase in the rate when present in the meta position, mainly due to its electron releasing inductive effect. When present in the para position, mesomeric electron release due to the hyperconjugation effect also comes into play, resulting in a greater electron release. Hence a higher rate is observed for p-methylphenoxyacetic acid. p-methoxyphenoxyacetic acid, due to the direct mesomeric interaction with the reaction centre, reacts faster than m-methoxyphenoxyacetic acid. The observed rates for chloro and bromo-substituted phenoxyacetic acids are in accordance with the inductive and mesomeric effects of the halogens. The influence of p-nitrophenoxyacetic acid on the reaction rate is as expected.

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