OXIDATION STUDIES—III

Oxidation of Ketone by Ceric Ions in Perchloric Acid

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Abstract

The oxidation of aliphatic unsymmetrical ketones-n-propyl methyl ketone and isobutyl methyl ketone and cyclic ketone-cyclohexanone by ceric perchlorate in perchloric acid ($\approx 0\cdot5$–$2\cdot0$ M) was studied in the temperature range $10°$–$30°$ C. The kinetics of the reactions were followed by measuring rate of Ce^{4+} disappearance effecting variations in $[Ce^{4+}]$, [Ketone], $[HClO_4]$, ionic strength μ, temperature, etc., and the reactions were found to be 2nd order—first order each with respect to $[Ce^{4+}]$ and [ketone]. No evidence for complex formation between Ce^{4+} and ketone was obtained from kinetics or by an independent absorptiometric method. Ce^{4+} (aq) and enol of the ketones were the active species for oxidation. Correlations between rates of enolisation of ketones and oxidation of the latter by Ce^{4+} were observed. The rate constants and their thermodynamic data were calculated and discussed. A mechanism based on the concept of oxidation as a process of successive hydroxylation of organic molecules is proposed.

Introduction

The oxidation of aliphatic ketones in solution by selenious acid,[1, 2] $KMnO_4$[3] and dichromate[4] was assumed to proceed through enolisation of ketones. Shorter and Hinshelwood[5] studied the oxidation of aliphatic ketones—acetone, methyl ethyl ketone, n-propyl methyl ketone, isobutyl methyl ketone, n-amyl methyl ketone, etc., with $Ce(SO_4)_2$ at $70°$ C. and correlated structure and enolisation constants of ketones with reactivity of the latter. In the oxidation of acetone by $Ce(SO_4)_2$ in H_2SO_4 and ceric ammonium nitrate in HNO_3, Shorter and Hinshelwood[6,7] concluded that the rate determining step involved the reaction between the enolic form of acetone and various sulphate complexes of Ce^{4+} in H_2SO_4 and $Ce(OH)^{3+}$ in HNO_3. We present results of our studies on the oxidation of cyclohexanone, n-propyl methyl ketone and isobutyl methyl ketone by ceric perchlorate in $HClO_4$ ($\sim0\cdot5$ to $2\cdot0$ M) in the temperature range $10°$–$30°$ C. Our observations may be

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best explained by the reaction, enolic form of ketone $+ Ce^{4+}$ (aq) in a slow step and rates of oxidation of the ketones are best interpreted in terms of rates of enolisation of the latter. In the oxidation of acetone and methyl ethyl ketone by Ce^{4+} in $HClO_4$, Venkatakrishnan and Santappa[8] assumed formation of intermediate complex between Ce^{4+} and the ketones but in the present study no evidence for such complex formation would be obtained from kinetics or by an independent absorptiometric method. The various rate constants and thermodynamic data were calculated and discussed.

EXPERIMENTAL

All solutions for kinetic studies were prepared in doubly distilled and deionised water. Ceric perchlorate solution (G. Frederick Smith Chemical Co., U.S.A.; 0·5 M in 5·0 M perchloric acid) was over 99·9% pure as tested from its ϵ at $\lambda = 290$ mμ[9] being $1·89 \times 10^3 M^{-1} cm.^{-1}$ The cyclohexanone, n-propyl methyl ketone and isobutyl methyl ketone (A. R., B.D.H.) were dried over anhydrous sodium sulphate, fractionally distilled and then used for our experiments. The perchloric acid (E. Merck; 70%) and sulphuric acid (Basynth, A. R., India; Sp. Gr. 1·8) were not further purified. The sodium perchlorate ($\approx 4·0$ M) was prepared by neutralisation of perchloric acid ($\approx 8·0$ M) with sodium hydroxide ($\approx 8·0$ M) and assayed by ion exchange method.[10] Cerous perchlorate was prepared by dissolving pure cerous carbonate (Atomic Energy Estd., India) in $HClO_4$ and the cerous content was estimated, after precipitation of the former as cerous oxalate and weighing and the free acid in cerous solution was estimated by ion exchange method.[10]

The reaction vessel was a three-necked pyrex flask (250 ml.; one B-24 middle and two B-19 side necks) fitted with mercury seal stirrer for the middle neck; one side-neck was used for bubbling nitrogen gas through the system while the 2nd neck for the exit of the gas and for withdrawing aliquots of the reaction mixture in the kinetic runs. The reaction system consisted of ceric perchlorate ($\sim 3·5 \times 10^{-3}$ M); ketone (cyclohexanone, 0·0096 M; n-propyl methyl ketone, 0·14 M and iso-butyl methyl ketone, 0·04 M); H^+ (1·0 M) with a total volume of 100 ml. and at an ionic strength, 1·2. All the components except Ce^{4+} were taken in the reaction flask which was thermostated (controlled by toluene regulator and a hot wire vacuum switch relay). Ceric solution was also thermostated in a separate flask at the same temperature. The ceric solution was added to the ketone solution, the time at which one-half of ceric solution was transferred being taken as the start of the reaction. The reaction was followed for 30 minutes to 40–50% conversion

of Ce^{4+} by measuring the rates of ceric disappearance at 5 minutes intervals—aliquots (10 ml.) withdrawn being added to known excess of Fe^{2+} sulphate solution ($\sim 3 \cdot 5 \times 10^{-3}$ M) using ferroin indicator.

The photochemical oxidation of water by ceric perchlorate is a well established fact[11] and therefore all the reactions were conducted with the reaction vessel covered with black cloth and the thermostat painted black inside. Absorption measurements made for the search for complex formation were carried out using u.v. spectrophotometer (H–700 type, Hilger and Watts).

RESULTS AND DISCUSSIONS

1. *Experimental results*:

(i) *Orders with respect to* $[Ce^{4+}]$ *and* $[Ketone]$.—At constant [Ketone] ($\approx 0 \cdot 0097$ M for cyclohexanone; $\approx 0 \cdot 14$ M for *n*-propyl methyl ketone and $\approx 0 \cdot 04$ M for iso-butyl methyl ketone) $[HClO_4] = 1 \cdot 0$ M, $\mu = 1 \cdot 2$, temperature ($20°$ C. for *n*-propyl methyl ketone; $25°$ C. for iso-butyl methyl ketone and $10°$ C. for cyclohexanone) and varying the $[Ce^{4+}]$ ($2 \cdot 5 \times 10^{-3}$ 5×10^{-3} M), a first order dependence with respect to $[Ce^{4+}]$ was observed for all the ketones (Fig. 1, A, B and C). From slopes of plots of log $[Ce^{4+}]$ *vs.* time
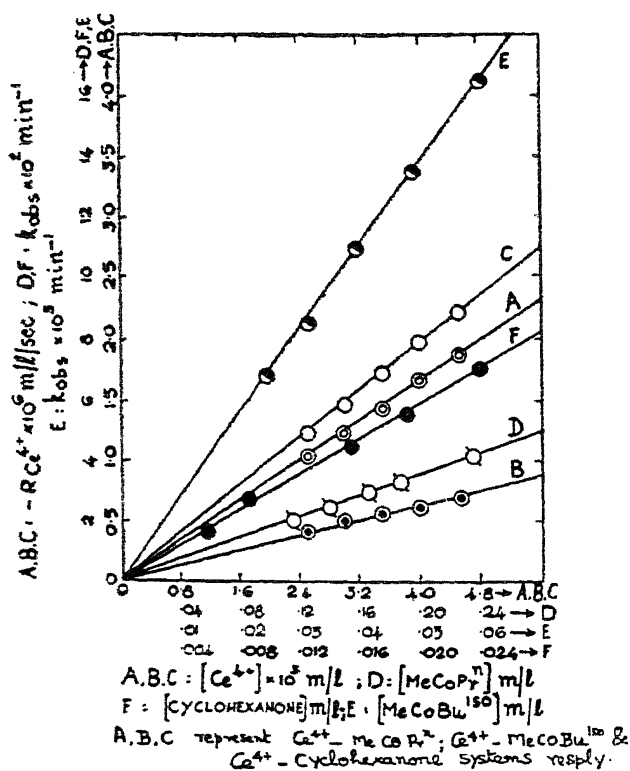

FIG. 1

pseudounimolecular rate constants, $k_{obs.}$, were calculated. At constant [Ce^{4+}] ($\approx 3 \cdot 5 \times 10^{-3}$ M), [HClO$_4$] $= 1 \cdot 0$ M, $\mu = 1 \cdot 2$ and temperature, and varying [Ketone] ($5 \cdot 79 \times 10^{-3}$ M $- 2 \cdot 41 \times 10^{-2}$ M for cyclohexanone; $0 \cdot 114$ M to $0 \cdot 24$ M for n-propyl methyl ketone and $0 \cdot 03$ M$-0 \cdot 06$ M for iso-butyl methyl ketone) a first order dependence with respect to [ketone] was observed for all the ketones studied (Fig. 1, D, E and F). That the total order was two for each Ce^{4+}-ketone system was confirmed from linear plots of $1/$[Ce^{4+}] *vs.* time (Fig. 2, D, E and F) under conditions [Ce^{4+}] $=$ [Ketone] (n-propyl
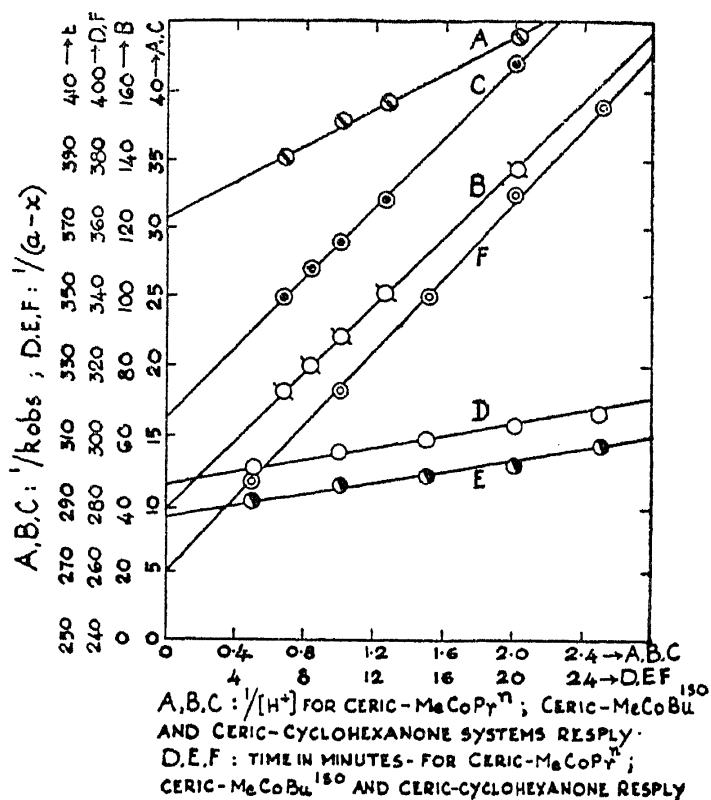

FIG. 2

methyl ketone or isobutyl methyl ketone) $\approx 3 \cdot 5 \times 10^{-3}$ M and [Ce^{4+}] $=$ [Cyclohexanone] $\approx 3 \cdot 86 \times 0^{-3}$ M in 1M HClO$_4$.

(ii) *Effect of* [H^+].—At constant μ, the rate of oxidation increased with increasing [H$^+$] ($0 \cdot 5$–$2 \cdot 0$ M) but at higher acidities ($> 2 \cdot 0$ M) the rate reached a limiting value. Plots of $1/k_{obs.}$ *vs.* $1/$[H$^+$] were linear with intercepts for all the ketones studied (Fig. 2, A, B and C).

(iii) *Effect of ionic strength,* μ.—Keeping constant [H$^+$] and varying μ ($1 \cdot 1$–$2 \cdot 0$) an increase of $10 ; 7$ and 2% in rate was observed for cyclohexanone, n-propyl methyl ketone and isobutyl methyl ketone respectively due to normal salt effects.

(iv) *Effect of initially added* [Ce^{3+}].—At constant [Ce^{4+}], [ketone], [H$^+$], μ, temperature, etc., initial addition of [Ce^{3+}] ([Ce^{3+}]/[Ce^{4+}] $\geqslant 2$) did not affect the rate of oxidation.

(v) No complex formation between Ce^{4+} and ketones was involved because plots of $1/k_{obs.}$ vs. $1/[ketone]$ (Fig. 3, D, E and F) passed through the
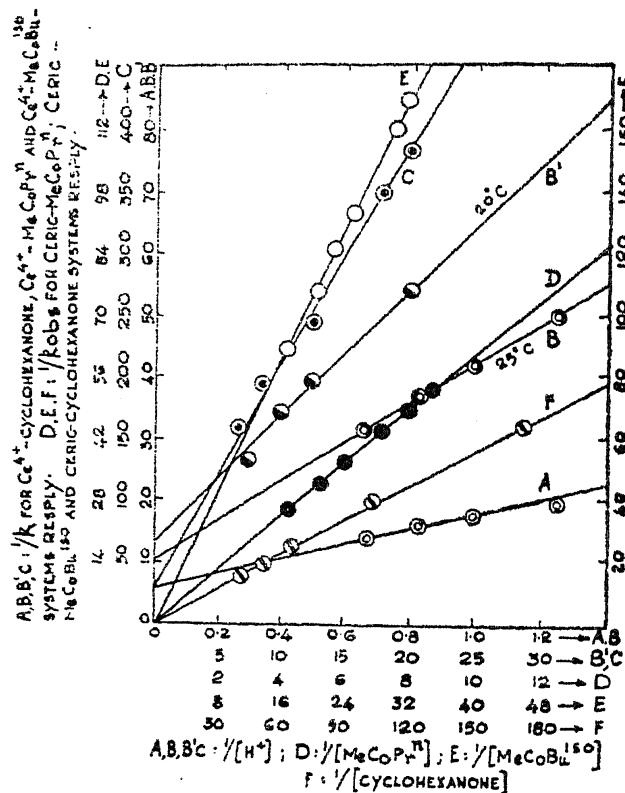

FIG. 3

origin with no intercepts. Had there been complex formation, such plots would have left intercepts (cf., Michaelis and Menten[12] and others[13-16]); no evidence for complex formation could be obtained from absorptiometry also and in fact no shift of the absorption peak for Ceric ion ($\lambda = 320$ mμ) at all was observed on adding excess [ketone] ([n-propyl methyl ketone] $\approx 2\cdot5 \times 10^{-2}$ M) to the solution of the former. Perhaps the concentrations of Ce^{4+} used in the present study were too low for complex formation to go to completion and to permit its detection.

(2) Mechanism of oxidation

The rates of oxidation of ketones by Ce^{4+} in $HClO_4$ were unaffected by initial addition of $[Ce^{3+}]$ to the system and therefore the possibility of oxidation by OH radicals produced in the possible equilibrium:
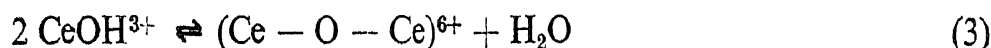
$$Ce^{4+} + H_2O \rightleftharpoons Ce^{3+} + H^+ + OH \tag{1}$$

might be ruled out. The forward reaction (1), viz., water oxidation by Ce^{4+}, was in fact negligible under our experimental conditions, as shown by blank

experiments. In all aqueous perchloric acid-Ce^{4+} systems, the hydrolytic equilibrium

$$Ce^{4+} + H_2O \overset{K_h}{\rightleftharpoons} Ce^{4+} OH^- + H^+ \qquad (2)$$
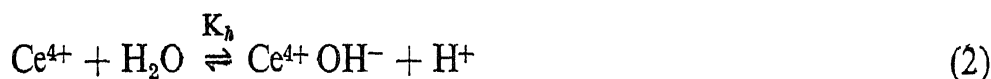
and dimerisation of hydrolysed species,

$$2\,CeOH^{3+} \rightleftharpoons (Ce - O - Ce)^{6+} + H_2O \qquad (3)$$

would be present, high $[H^+]$ ($< 4\cdot0$ M) favouring predominance of unhydrolysed Ce^{4+}; low $[H^+]$ and low $[Ce^{4+}]$ contributing to Ce^{4+} OH^- and very high $[Ce^{4+}]$ favouring dimeric species.[17] Since $[Ce^{4+}] \approx 10^{-3}$ M and the acidity used was $1\cdot0$ M dimers of Ce^{4+} may be neglected and Ce^{4+} as well as Ce^{4+} OH^- would be present in our systems and since the rate increased with increasing $[H^+]$ (Fig. 3; A, B and C) the unhydrolysed species Ce^{4+} and the enolic form,
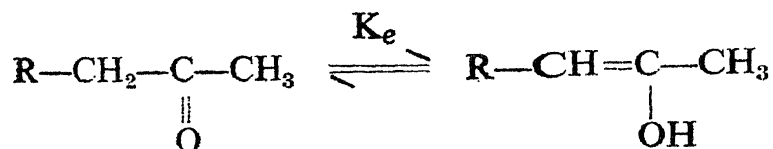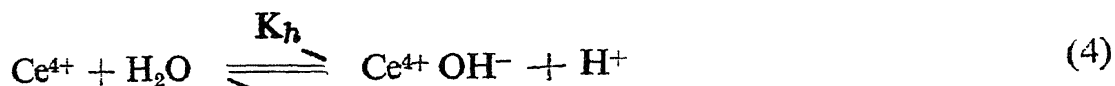
$$R-\overset{\overset{\displaystyle OH}{|}}{C}=CH_2 \quad \text{or} \quad R'-CH=\overset{\overset{\displaystyle OH}{|}}{C}-CH_3,$$

of ketone would be the active species. If the negative ion ($R-CO-Me \rightleftharpoons R-CO-CH_2^- + H^+$) were active, the rate would have been inversely proportional to $[H^+]$ which was contrary to our observation. Neutral form of ketone may therefore be the most probable active species. Enol form of ketone was suggested as active species in the oxidation of ketones by Shorter[5-7] and others.[1-4] The relative rates of acid catalysed enolisations for various ketones were measured by Dawson[18] and Jones[19] by halogenation method and the values of the over-all rates of enolisations (with acetone as the standard) and the rates of enolisations at α-CH_3, α-CH_2 and α-CH positions in the various ketones were calculated by Jones.[19] On the basis of the values for rates of enolisation given by Jones,[19] Shorter[6, 7] correlated in a more quantitative way, the rate of oxidation of acetone by Ce^{4+} with its rate of enolisation. The ratio of rates of enolisation[19] of n-propyl methyl ketone and isobutyl methyl ketone at α-CH_3 position $\approx 0\cdot87$; at α-CH_2 position $\approx 1\cdot303$ and for the over-all enolisation $\approx 1\cdot092$. Our value for the ratio of rates of oxidation of n-propyl methyl ketone and isobutyl methyl ketone being $1\cdot33$ at $35°$ C., the correlation between oxidation and enolisation at α-CH_2 position is obvious and hence unsymmetrical

ketones enolising at α-CH_2 position, $R-CH=\overset{\overset{\displaystyle OH}{|}}{C}-CH_3$ must be the active species in our systems. The extensive enolisation of cyclohexanone as compared to acetone and cyclopentanone was reported by various workers.[20-22] It is therefore reasonable to assume that the oxidation

of the ketones studied occurred between the enolic form of the ketones and Ce^{4+} (aq). The whole course of the reaction may be represented as follows:

$$Ce^{4+} + H_2O \xrightleftharpoons{\quad K_h \quad} Ce^{4+} OH^- + H^+ \tag{4}$$

$$R-CH_2-\underset{\underset{O}{\parallel}}{C}-CH_3 \xrightleftharpoons{\quad K_e \quad} R-CH=\underset{\underset{OH}{\mid}}{C}-CH_3 \tag{5}$$

or

$$\tag{5}$$

$$Ce^{+4} + R-CH=\underset{\underset{OH}{\mid}}{C}-CH_3 \xrightarrow[\text{slow}]{k'} \dot{R} + Ce^{3+} \tag{6}$$

$$Ce^{4+} + \dot{R} + H_2O \xrightarrow{\text{fast}} Ce^{3+} + \text{Products} \tag{7}$$
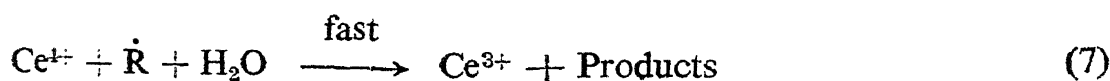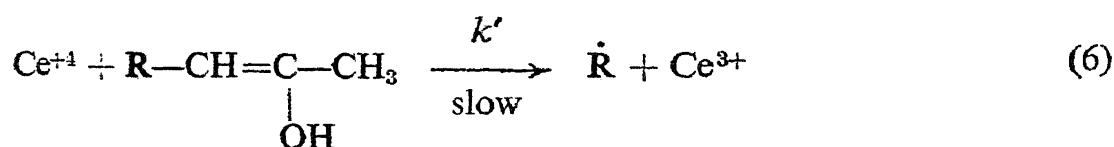
where $\dot{R}$ is an active intermediate free radical of ketone.

It follows that the rate of reaction would be

$$\frac{-d[Ce^{4+}]}{dt} = k'[Ce^{4+}][Enol] = k[Ce^{4+}]_T[ketone]_T \tag{8}$$

k, k' being the observed and theoretical rate constants; $[Ce^{4+}]$ the unhydrolysed ceric species; $[Ce^{4+}]_T$ and $[ketone]_T$ representing the total concentrations. It also follows that

$$\frac{1}{k} = \frac{1}{k'} + \frac{1}{k'K_e} + \frac{K_h}{k'[H^+]} + \frac{K_h}{k'K_e[H^+]} \tag{9}$$

plots of $1/k$ vs. $1/[H^+]$ (Fig. 3; A, B and C) were linear and from the slope/ intercept on the ordinate, K_h values (Table I) obtained were in good agreement with those reported by Hardwick and Robertson.[17] Assuming K_e values (Eqn. 9) in $HClO_4$ at α-CH_2 position for the unsymmetrical ketones, viz., n-propyl methyl ketone and isobutyl methyl ketone to be the same as in H_2SO_4 by Jones,[19] values of k' for both the ketones were evaluated from the intercept of $1/k$ vs. $1/[H^+]$ plots (Table I).

TABLE I

Evaluation of K_h, k' and k

Substrate	Temp. °C.	K_h^*	k'	k (1 moles^{-1} sec.$^{-1}$)
n-Propyl methyl ketone ...	25	5·00	0·054	$4·77 \times 10^{-3}$
Isobutyl methyl ketone ..	25	5·40	0·088	$3·6 \times 10^{-3}$
Cyclohexanone ..	10	1·43	...	$4·75 \times 10^{-2}$

* K_h at 25° C[17] $\sim$ 5·2 and 10° C[16] — 1·5.

(3) *Rate and thermodynamic data and their interpretation*

The thermodynamic data for the oxidation of ketones by Ce^{4+} in $HClO_4$ medium are summarized in Table II.

TABLE II

Thermodynamic parameters for k

Substrate	$\triangle E$ K. Cal/mole.	$\triangle S^{\pm}$ e.u.	$\triangle F^{\pm}$ K.Cal/mole.
n-Propyl methyl ketone ...	17·7	−11·7	21·12
Isobutyl methyl ketone	14·2	−24·3	21·39
Cyclohexanone	21·8	10·3	18·84

The higher rate of oxidation of *n*-propyl methyl ketone over isobutyl methyl ketone may be due to higher rate of enolisation (at α-CH_2 position) in the former. In cyclohexanone the over-all rate of enolisation is greater and hence the maximum rate. The constancy in $\triangle F^{\pm}$ for *n*-propyl methyl ketone and isobutyl methyl ketone may be explained on the basis of isokinetic relationship[23] that for a series of compounds of slightly different structure but undergoing reaction by the same mechanism, the $\Delta F^{\dagger}$ may be more or less constant with relative changes in $\triangle E$ and $\triangle S^{\pm}$. The change in $\Delta S^{\pm}$ values for cyclohexanone as compared to *n*-propyl methyl or isobutyl methyl ketones suggests difference in the structures for the two in the transition state. The

negative $\triangle S^{\pm}$ values for the two unsymmetrical ketones studied, may be explained in terms of the transition state theory that for a reaction involving two atoms or simple molecules there is a relatively small rearrangement of energy between the various degrees of freedom in the formation of the activated state and in these circumstances $\triangle S^{\pm}$ will be negative or positive.

(4) Course of oxidation of ketones

A mechanism based on the concept of oxidation of organic molecules as a process of successive hydroxylation similar to that invoked by Shorter[5-6] for unsymmetrical ketones may also be extended to Cyclohexanone, a typical cyclic ketone:
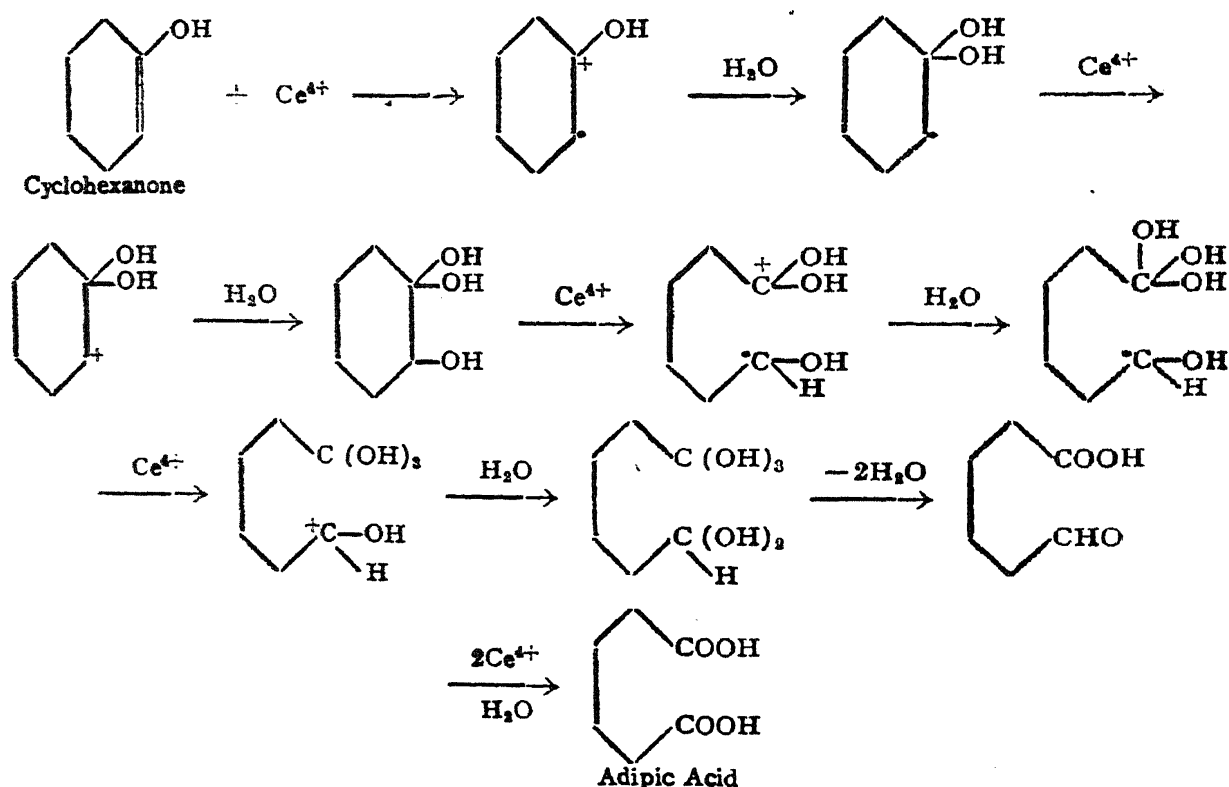
ACKNOWLEDGEMENT

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