Oxidation of Alcohols by Cerium(IV). I. Oxidation of Methanol by Ceric Perchlorate

By S. S. MUHAMMAD and K. Vijayachander RAO

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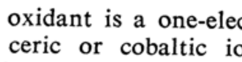
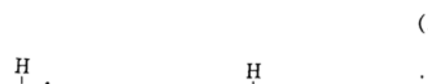
The oxidation of alcohols belongs to the category of reactions in which electron transfer is accompanied by the fission of one or more covalent bond:



$$CH_3\text{-}\overset{H}{\underset{H}{C}}\text{-}O\text{-}H \xrightleftharpoons{-2H} CH_3\text{-}\overset{H}{C}{=}O \qquad (A)$$

When the oxidant is a one-electron abstractor such as a ceric or cobaltic ion, these reactions involve the formation of free radicals, as pointed out by Dainton[1] in his Tilden lecture. Thus the work of Bawn and White[2,3] on the oxidation of formic acid, formaldehyde and methanol by cobaltic ions and the work of Mino, Kaizerman and Rasmussen[4] on the oxidation of pinacol by ceric sulfate demonstrated the formation of the free radicals. For example in the oxidation of ethanol by ceric ions the following reactions take place:



$$CH_3\text{-}\overset{H}{\underset{H}{C}}\text{-}O\text{-}H + Ce^{4+} = CH_3\text{-}\overset{H}{\underset{H}{C}}\text{-}\dot{O} + H^+ + Ce^{3+} \qquad (A1)$$

$$CH_3\text{-}\overset{H}{\underset{H}{C}}\text{-}\dot{O} + Ce^{4+} = CH_3\text{-}\overset{H}{C}{=}O + H^+ + Ce^{3+} \qquad (A2)$$

which conform to the observed stoichiometry of 2 ceric ions for one alcohol molecule.

On the basis of his kinetic studies on the trivalent manganese-oxalate reaction[5] and the oxidation[6] of acetone by selenious acid, Duke developed the theory of specific oxidation of glycols and related compounds. He assumed that coordination intermediates[7] are first formed through rapidly established equilibrium between the oxidant and the reductant and thence a slow disproportionation of these complexes occurs. The oxidation of 2, 3-butanediol by nitrato cerate was shown by Duke and Forist[8] to proceed through the disproportionation of a monoglycollated coordination intermediate. Similarly, in their study of the oxidation of meso-2, 3-butanediol (G) by ceric perchlorate, Duke and Bremer[9] noticed the formation of complexes such as $\{Ce\,G(H_2O)_4\}^{4+}$, and $\{Ce\,G_2(H_2O)_2\}^{4+}$ which then decomposed unimolecularly. Later Ardon's[10] investigation of the oxidation of ethanol by ceric ions in perchloric acid showed that the reaction occurred in two consecutive steps, similar to the scheme of Duke. He also established the existence of a 1-1 cerate-alcohol complex independently by a spectrophotometric method. Further, Venkatakrishnan and Santappa[11] found that the oxidation of acetone and methylethyl ketone via the formation of a

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[1] F. S. Dainton, *J. Chem. Soc.*, **1952**, 1537.

[2] C. E. H. Bawn and A. C. White, ibid., **1951**, 323, 331, 343.

[3] C. E. H. Bawn and A. C. White, *Discussions Faraday. Soc.*, **14**, 181 (1953).

[4] G. Mino, S. Kaizerman and E. Rasmussen, *J. Am. Chem. Soc.*, **81**, 1494 (1959).

[5] F. R. Duke, ibid., **69**, 2855 (1947).

[6] F. R. Duke, ibid., **70**, 419 (1948).

[7] Similar views were also expressed by H. Taube: ibid., **70**, 1216 (1948).

[8] F. R. Duke and A. A. Forist, ibid., **71**, 2790 (1949).

[9] F. R. Duke and R. F. Bremer, ibid., **73**, 5179 (1951).

[10] M. Ardon, *J. Chem. Soc.*, **1957**, 1811.

[11] S. Venkatakrishnan and M. Santappa, *Z. physik. Chem.* (*N. F.*), **16**, 1-2, 93 (1958).

complex between the ceric ions and enolic form of acetone.

On the other hand, several studies⑫ using ceric sulfate as oxidant in the oxidation of acetone, formaldehyde, alcohols and hydroxy-acids have given no indication of any intermediate complex formation. Hence it appeared of interest to investigate the divergence of behavior of ceric perchlorate and ceric sulfate, using methanol as the substrate under varying conditions of reagent concentration, acidity and temperature.

The first part contains our data on the oxidation of methanol by ceric perchlorate and this will be followed by the results in presence of ceric sulfate in Part II.

Experimental Method and Results

All the chemicals used were analar and of highest purity. Ceric perchlorate was prepared by the anodic oxidation of cerous perchlorate. This was obtained by dissolving the freshly precipitated ceric hydroxide in perchloric acid and reducing the resulting ceric perchlorate by adding concentrated hydrogen peroxide. The colorless solution of cerous perchlorate was electrolyzed with a current of 3 amp. at 4 V., using a platinum hood as the cathode and a platinum wire as the anode, the temperature of the electrolytic bath being maintained at 0°C. The solution of ceric perchlorate obtained had a strength of 0.01 M approximately and could be diluted to desired extent. For each series of experiments, ceric perchlorate was freshly prepared and it was not allowed to age long, as Vickery⑬ asserts that aged solutions develop hydrosols and become less reactive.

Methanol was analar reagent grade. The formaldehyde produced was identified and estimated by Schiff's and Schryver's reagents. In the latter case, a photometric calibration curve was constructed with standard solutions of formaldehyde with the Schryver's reagent. All aqueous solutions were prepared with twice distilled water free from oxidizable impurities.

The reaction study was conducted in an all glass quickfit apparatus, having three jointed necks. Through the middle neck passed mercury seal stirrer, the second allowed nitrogen gas in the reacting system, while the third neck was used for the solutions to be put in or taken out by means of a pipette. During reaction, the latter two were closed by ground glass stoppers.

To maintain temperature, a Gallen Kamp thermostat with a toluene regulator was used, the range of fluctuations being ±0.1°C. For temperatures lower than the room temperature ice cold water was circulated in lead coils in the bath.

The colorimetric estimation of cerium(IV) or formaldehyde was carried out on a Bosh & Lomb's Spectronic 20 type colorimeter, while the complex study was done on a Unicam spectrophotometer, model Sp 500.

The photochemical and thermal oxidation of water by ceric perchlorate is a well established fact⑭. Hence experiments were conducted in a dark room; the reaction vessel was covered with a black cloth. Blank experiments were also done and corrections were applied wherever necessary.

The rate of oxidation was followed by the rate of disappearance of ceric perchlorate, which was measured by adding excess of standardized ferrous ammonium sulfate solution and titrating the unreacted ferrous ion by standard ceric sulfate in presence of methyl red as indicator. Preliminary experiments showed that the volumetric titration was as accurate as the photometric estimation. Besides it was more suitable than the potentiometric titration which took longer time.

Stoichiometry and Order of Reaction.—The reaction mixture containing different proportions of reactants were analyzed after different intervals both for formaldehyde and for ceric perchlorate. The results are given in Table I.

TABLE I. STOICHIOMETRY OF THE REACTION
Temp., 20°C; 1.0 M perchloric acid

MeOH $\times 10^2$ M	Ce^{4+} $\times 10^{+3}$ M	$-\Delta Ce^{4+}$ $\times 10^3$ M per min.	$+\Delta HCHO$ $\times 10^3$ M per min.
2.0	3.55	0.56	0.26
3.0	3.55	0.82	0.40
5.0	3.55	1.32	0.63
6.0	3.55	1.58	0.75
10.0	3.55	2.48	1.20

In each case formaldehyde formed (or methyl alcohol consumed) is nearly half of the ceric ions disappearing in a given time. Hence the stoichiometry is "2 ceric 1 alcohol".

Using different initial amounts of ceric perchlorate with 0.11 M methanol and 1.0 M perchloric acid, the rate of disappearance of ceric ions was found to be directly proportional to ceric ions concentration. Further log Ce^{4+}-time graph was a straight line, confirming the first order dependence of rate on the ceric ion concentration. The latter graph was generally used to derive the rate constants.

Keeping ceric perchlorate at 3.55×10^{-3} M in a molar perchloric acid at 20°C and changing the concentrations of methanol between 0.01 to 0.50 M, it was found that the rate of oxidation rises with increase of methanol concentration, but tends to reach a limiting value at high concentrations of methanol. This is clear from the plot of rate of oxidation vs. methanol concentration shown in Fig. 1a. Figure 1b is the plot of log relative rate against log

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⑫ See part II: This Bulletin, **36**, 949 (1963).

⑬ R. C. Vickery, "Chemistry of Lanthones", Butterworths, London (1953), p. 233.

⑭ See for example: a) L. J. Heidt and M. E. Smith, *J. Am. Chem. Soc.*, **70**, 2476 (1948); b) Don Kolp and H. C. Thomas, ibid., **71**, 3047 (1949); c) F. B. Baker, T. W. Newton and M. Kahn, *J. Phys. Chem.*, **64**, 109 (1960).

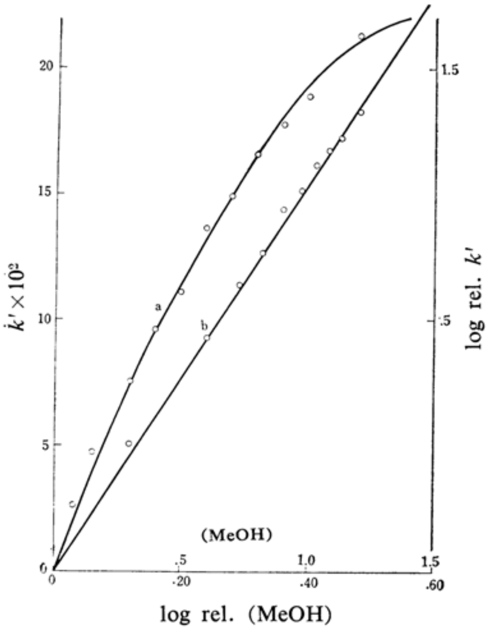


Fig. 1. Effect of methanol concentration.
a k' vs. (MeOH)
b log rel. k' vs. log rel. (MeOH)

relative methanol concentration and has a slope of 0.77.

Effect of Acid and Ionic Strength.—Experiments at constant ionic strength showed that at low acidities the rate is proportional to acid concentration, but at high acidities, it reaches a maximum value (Table II).

TABLE II. EFFECT OF ACID CONCENTRATION AT CONSTANT IONIC STRENGTH
$Ce^{iv} = 3.55 \times 10^{-3}$ M, methanol = 0.11 M, $\mu = 2.504$ M and $T = 20°C$

$HClO_4$ M	$k' \times 10^2$ min^{-1}	$1/HClO_4$	$1/k'$
0.75	7.37	1.33	13.57
1.00	8.64	1.00	11.58
1.25	9.67	0.80	10.39
1.50	10.36	0.67	9.63
2.00	10.70	0.50	9.35
2.50	11.40	0.40	8.77
3.00	11.60	0.33	8.62

If the reciprocals of the rate constants are plotted against the reciprocals of the acid concentration, a straight line results. But keeping the acid concentration the same and varying the amount of added sodium perchlorate (Table III) it was found that the reaction has a normal salt effect.

The variations of the rate constants in the range 7∼27°C are shown in Table IV.

The activation plot yields 14.45 kcal./mol. as the apparent activation energy.

TABLE III. INFLUENCE OF IONIC STRENGTH AT CONSTANT ACIDITY
$Ce^{iv} = 3.55 \times 10^{-3}$ M, methanol = 0.11 M, $HClO_4 = 1.0$ M and $T = 20°C$

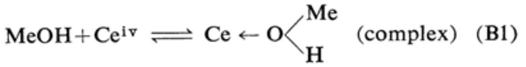
Lot of $NaClO_4$ in 50 cc.	Total ionic strength	$k' \times 10^2$ min^{-1}		$\log k' + 2$
0.0000	1.030	8.60	1.015	0.9345
0.2385	1.069	8.94	1.034	0.9513
0.4770	1.108	9.21	1.052	0.9643
0.7200	1.148	9.44	1.072	0.9750
0.9542	1.186	9.81	1.089	0.9917
1.1922	1.226	10.17	1.108	1.0072
1.4298	1.264	10.60	1.124	0.0251

TABLE IV. VARIATIONS OF RATE CONSTANTS WITH TEMPERATURE
$Ce^{iv} = 3.55 \times 10^{-3}$ M, methanol = 0.11 M, $HClO_4 = 1.0$ M

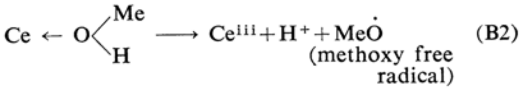
Temp. °C	First order rate constant (each constant is the mean of three experiments)	Mean $k' \times 10^2$ min^{-1}
7	0.027, 0.026, 0.029	2.73
13	0.050, 0.044, 0.053	4.90
20	0.088, 0.086, 0.087	8.70
27	0.174, 0.188, 0.164	17.53

Discussion

The present data on the oxidation of methanol are directly in line with the findings of Duke and Bremer[9] and Ardon[10] and may be explained on similar lines. Hence we invoke Duke's mechanism and assume that methanol in perchloric acid medium is oxidized by cerium(IV) only after complex formation:



$$MeOH + Ce^{iv} \rightleftharpoons Ce \leftarrow O\begin{smallmatrix}Me \\ H\end{smallmatrix} \quad \text{(complex)} \qquad (B1)$$



$$Ce \leftarrow O\begin{smallmatrix}Me \\ H\end{smallmatrix} \longrightarrow Ce^{iii} + H^+ + Me\dot{O} \qquad (B2)$$

(methoxy free radical)

These reactions are of course followed by a very fast step in which the methoxyl free radical reacts with another ceric ion:

$$Me\dot{O} + Ce^{iv} \longrightarrow Ce^{iii} + HCHO + H^+ \qquad (C)$$

which accounts for the observed stoichiometry, 2 ceric: 1 methanol. But the last step being very fast is out side the scope of the present study.

State of Ce^{iv} in Perchloric Acid.—In order to elucidate Duke's mechanism we require a knowledge of (1) the state of Ce^{iv} in perchloric acid, (2) the complex or complexes formed and (3) the disproportionation of these complexes.

Hardwick and Robertson[15] have shown that

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[15] T. J. Hardwick and E. Robertson, *Canad. J. Chem.*, **29**, 818 (1951). See also, E. L. Ring and M. L. Pandow, *J. Am. Chem. Soc.*, **74**, 1966 (1952).

in aqueous perchloric acid solutions of ceric perchlorate three ionic species Ce^{4+}, $CeOH^{3+}$, and $(Ce-O-Ce)^{6+}$ can exist, comprising the reactions:

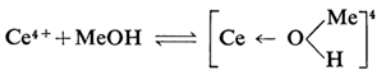
$$Ce^{4+}+H_2O \rightleftharpoons CeOH^{3+}+H^+ \qquad (D)$$

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

High acidity favors the Ce^{4+} ions, though very high acidities (probably above 4 M) have to be avoided, for according to Vickery[13], autoreduction may occur. In low acidity and dilute solutions, the hydrolyzed form predominates. But increase in total ceric concentration helps the dimerization process and if acidity is also low, Ardon and Stein[16] state that irreversible colloidal polymers are also formed. As the ceric concentration in the present work was of the order of 10^{-3} M, the existence of the binuclear species $Ce\text{-}O\text{-}Ce^{6+}$ may be neglected and we take the reactive species to be unhydrolyzed Ce^{4+} as done by Duke and Bremer[9] and Ardon[10]. Our observation that the rate of oxidation increases though slowly, by rise in perchloric acid concentration in the range 1.0 to 3.5 M, is in conformity with the equilibrium D, in which higher acidity should favor the existence of the unhydrolyzed monomeric species Ce^{4+}. This may actually be the hexahydrated ion $Ce(H_2O)_4^{4+}$, for which the symbol Ce^{4+} will be used in later treatment.

Cerium(IV)-Methanol Complexes. — The coordination complexes between ceric perchlorate and methanol may be formed as a result of the displacement of perchlorate or water. Observed positive salt effect rules out any displacement of perchlorate by alcohol molecules. If the latter were correct, increasing addition of perchlorate would have decreased the rate. Hence it may be concluded that the displacement of coordination water by methanol molecules from Ce^{iv} occurs. The possible complexes would be $\{Ce\,X_5\cdot MeOH\}^{4+}$; $\{Ce\,X_4\,(MeOH)_2\}^{4+}$; $\{Ce\,X_3\,(MeOH_3)_3\}^{4+}$; $\{Ce\,X_2\,(MeOH)_4\}^{4+}$; $\{Ce\,X\,(MeOH)_5\}^{4+}$ and $\{Ce\,(MeOH)_6\}^{4+}$. Further since in solution $Ce\,OH^{3+}$ also exists, complexes such as $\{Ce(OH)X_4MeOH\}^{3+}$; $\{Ce(OH)X_3(MeOH)_2\}^{3+}$; $\{Ce(OH)\,X_2\,(MeOH)_3\}^{3+}$; $\{Ce(OH)\,X\,(MeOH)_4\}^{3+}$ and $\{Ce(OH)\,(MeOH)_5\}^{3+}$ are also possible. But according to Duke and Bremer, the latter type of complexes can not exist in appreciable amount in solution, for the hydrolyzed species has been found to be unimportant in the oxidation reaction.

Complex Formation and Disproportionation.— In the reaction:



$$Ce^{4+}+MeOH \rightleftharpoons \left[Ce \leftarrow O\begin{matrix}Me\\H\end{matrix}\right]^{4+} \qquad (F)$$

if the equilibrium concentrations are put as $Ce^{4+}=c-x$; (complex) $=x$; MeOH $=B$ (where methanol being in excess, its initial concentration is supposed to remain unchanged) the equilibrium constant

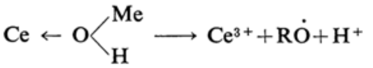
$$K=\frac{x}{(c-x)B} \qquad (1)$$

This gives

$$x=\frac{KBc}{1+KB} \qquad (2)$$

$$\text{or (complex)}=\frac{K(MeOH)(Ce^{4+})}{1+K(MeOH)} \qquad (3)$$

The rate of disproportionation of the complex:



$$Ce \leftarrow O\begin{matrix}Me\\H\end{matrix} \longrightarrow Ce^{3+}+R\dot{O}+H^+ \qquad (G)$$

$$\frac{-d\,Ce^{4+}}{dt}=k\ (\text{complex}) \qquad (4)$$

But using complex concentration from 3,

$$\frac{-d\,Ce^{4+}}{dt}=\frac{kK(MeOH)(Ce^{4+})}{1+K(MeOH)} \qquad (5)$$

This may be written as

$$\frac{-2.303\ d\log Ce^{iv}}{dt}=\frac{kK(MeOH)}{1+K(MeOH)} \qquad (6)$$

because the concentration of Ce^{4+} directly depends on total cerium(IV), which is the quantity measured experimentally. It shows that in any given experimental condition, the plot of log Ce(IV) vs. time will be a straight line, the slope of which multiplied by 2.303 gives the first order constant k', which varies with methanol concentration in the manner of Eq. 6. Hence

$$k'=\frac{kK(MeOH)}{1+K(MeOH)} \qquad (7)$$

or

$$\frac{1}{k'}=\frac{1+K(MeOH)}{kK(MeOH)}=\frac{1}{k}+\frac{1}{kK(MeOH)} \qquad (8)$$

It means that the plot of the reciprocal of the apparent rate constant against the reciprocal of methanol concentration is a straight line with an intercept (Fig. 2). This intercept is equal to $1/k$ and the slope $1/kK$, thus enabling us to evaluate the constants of cerate-methanol complex formation and of its disproportionation in different experimental conditions.

Equation 8 may also be used as an evidence for the formation of an intermediate complex in a reaction. It may be noted here that it

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[16] M. Ardon and G. Stein, *J. Chem. Soc.*, **1956**, 104.

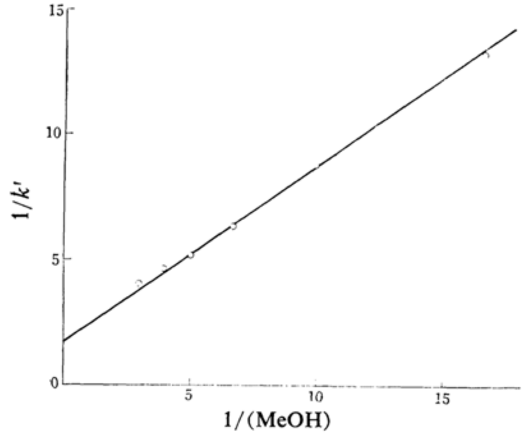

Fig. 2. Evidence for complex formation. Kinetic data.

is similar to Lineweaver and Burke's[17] equation which was a modification of the equation of Michaelis and Menton[18]. In order to explain the widely observed fact that the rate of an enzyme catalyzed reaction increased with the concentration of the substrate as a rectangular hyperbola and eventually levelled off a symptotically (compare Fig. 1), Michaelis and Menton suggested that the substrate combined with the enzyme to form a transient intermediate which then broke down to products:

$$\text{Enzyme}+\text{Substrate} \rightleftharpoons \text{Complex} \rightarrow \text{Products}+\text{Enzyme}$$

Hence Lineweaver and Burke showed that in the above case, if the reciprocal of the apparent velocity was plotted against the reciprocal of the concentration of the substrate, then a slope and intercept relation resulted. The graph of Fig. 2 gives 1.36 l. mol^{-1} as the stability constant at 20°C and 1.0 M perchloric acid.

To understand the proposed mechanism, the structure of the cerate-methanol complex should be known. Job's method being unsuitable here, Ardon's optical method based on the spectrophotometric method of Hildebrand and Benesi[20] was employed. In this method the plot of $(1/D-CE_a)$ against 1/(methanol) at 400 mμ gives a straight line with an intercept, provided 1 : 1 complex is formed between ceric and methanol. Here D is the optical density of the equilibrium mixture and C and E_a the concentration and molecular extinction coefficient of the colored species ceric ions. When all the mixtures observed are made to have the same volume, the measured optical density D' of the ceric ions may be used in place of CE_a. Figure 3 shows the graph of $1/(D-D')$ against 1/(methanol). The value of the formation constant is 2.97 at 20°C and 3.0 M acid.

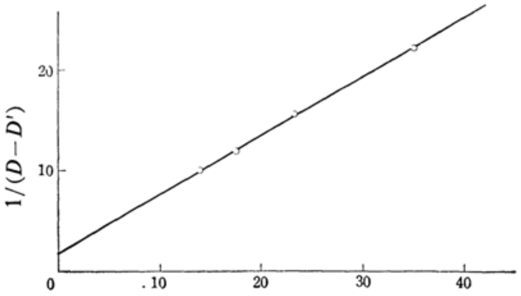

Fig. 3. Spectrophotometric data.

As the method of Ardon is based on the assumption that 1 : 1 complex is formed, it may be concluded that only 1 : 1 cerate-methanol is important in our experimental condition.

Effect of Acid Concentration. — If complex formation is represented by

$$\text{Ce}^{\text{iv}}+\text{MeOH} \rightleftharpoons (\text{Ce}^{\text{iv}}\cdot\text{MeOH})$$

and initial $\text{Ce(IV)}=\text{Ce}_0\text{(IV)}$ and at equilibrium the complex $=X'$, then the equilibrium constant,

$$K=\frac{X'}{(\text{Ce}^{\text{iv}}-X')(\text{MeOH})} \tag{10}$$

where it has been assumed that methanol being in excess, its concentration remains unchanged. But the reactive species being Ce^{4+}, the complex formation actually consists of reaction F:

$$\text{Ce}^{4+}+\text{MeOH} \rightarrow (\text{Ce}\cdot\text{MeOH})^{4+} \tag{F}$$

and the equilibrium constant $\overline{K}$

$$\overline{K}=\frac{X}{(\text{Ce}^{4+}-X)(\text{MeOH})} \tag{11}$$

In this equation Ce^{4+} is not equal to Ce^{iv} and $\overline{K}$ may be called the true stability constant, while K is the apparent stability constant.

In identical conditions of concentrations, acidity and temperature, the quantities X and X' may not be much different and we may assume them to be equal. Hence

$$\frac{\overline{K}}{K}=\frac{\text{Ce}^{\text{iv}}}{\text{Ce}^{4+}} \tag{12}$$

But $\text{Ce}^{\text{iv}}(\text{total})=\text{Ce}^{4+}+\text{CeOH}^{3+}$ in conditions where binuclear species are negligible and

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[17] H. Lineweaver and D. Burke, *J. Am. Chem. Soc.*, **56**, 81 (1934).

[18] L. Michaelis and M. Menton, *Bioch. Zeit.*, **49**, 333 (1913).

[19] P. Job, *Ann. chim.* (*France*), **9**, 113 (1928).

[20] J. H. Hildebrand and H. A. Benesi, *J. Am. Chem. Soc.*, **71**, 2703 (1949):

$$\frac{\overline{K}}{K}=\frac{Ce^{4+}+CeOH^{3+}}{Ce^{4+}}=1+\frac{CeOH^{3+}}{Ce^{4+}}$$

and from equilibrium of Eq. D, $CeOH^{3+}/Ce^{4+}=K_h/H^+$, where K_h is the hydrolysis constant. This gives

$$\frac{\overline{K}}{K}=1+\frac{K_h}{H^+}$$

or

$$\frac{1}{K}=\frac{1}{\overline{K}}+\frac{K_h}{\overline{K}\cdot H^+} \qquad (13)$$

This means that a plot of the reciprocal of the apparent stability constant (derived from Fig. 4) against the reciprocal of the acid concentration, yields a straight line with an intercept$=1/\overline{K}$ and a slope$=K_h/\overline{K}$. Table V incorporates our data on the variation of the rate constants at different acidities by changes of methanol concentration at 20°C and constant cerium(IV) concentration.

TABLE V. VARIATION OF RATE CONSTANTS AT DIFFERENT ACIDITIES BY CHANGING METHANOL AT 20°C

MeOH mol. l.	$k'\times10^2$ min^{-1}	1/MeOH	$1/k'$
		$HClO_4=1.00$ M	
0.03	2.60	33.30	38.42
0.06	4.79	16.67	20.79
0.11	8.68	9.10	11.63
0.24	16.58	4.17	6.03
		$HClO_4=2.00$ M	
0.05	6.70	20.00	14.93
0.06	7.69	16.67	13.00
0.10	11.51	10.00	8.69
0.15	15.76	6.67	6.34
		$HClO_4=3.50$ M	
0.05	9.26	20.00	10.80
0.08	12.74	12.50	7.85
0.15	20.90	6.67	4.79
0.20	26.30	5.00	3.80

The plot of 1/(methanol)-1/(rate constants) is shown in Fig. 4. It is interesting to note from this graph that while apparent stability constants decrease with decreasing acid concentration, the constant of disproportionation remains the same at different hydrogen ion concentrations. This proves that there is only one complex that decomposes.

Figure 5 shows a plot of the reciprocal of the apparent stability constant (as derived from Fig. 4) against the reciprocal of acid concentration. This yields the following values at 20°C:

True stability constant $\overline{K}=6.67$
Hydrolytic constant $K_h=3.75$

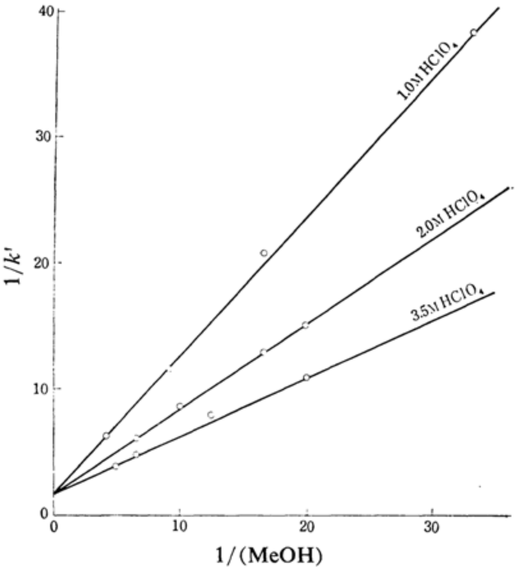


Fig. 4. Rate constants at different acidities at several methanol concentrations.

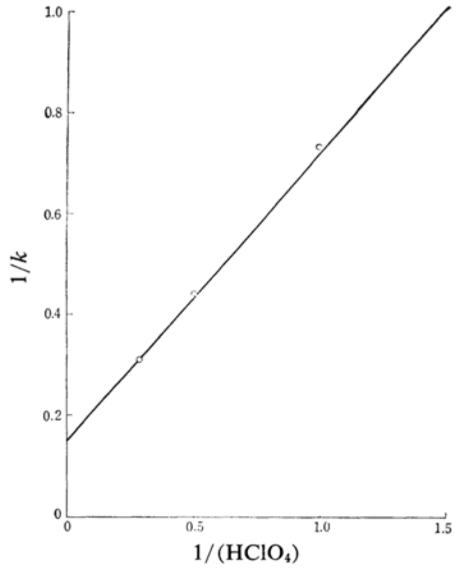
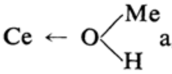


Fig. 5. Evaluation of hydrolytic constant and true formation constant.

The latter value closely agrees with Hardwick and Robertson's value 3.40. It has to be noted that though the apparent formation constant K decreases with decreasing acid concentration, the true formation constant $\overline{K}$ remains unchanged. Measurements at two temperatures yield the following values:

Temp.	K at 2.0 M acid	$\overline{K}$	K_h
13°C	3.74	7.21	1.85
20°C	2.34	6.67	3.57

while the apparent stability constant K has a temperature coefficient of 1.60 (for 7°C rise), that for the true stability constant is only 1.08. The former corresponds to a value of $\Delta H=$ 11.0 kcal. and the latter to about 2.0 kcal. This small heat of formation for the complex  $\mathrm{Ce} \leftarrow \mathrm{O}\genfrac{}{}{0pt}{}{\mathrm{Me}}{\mathrm{H}}$ again indicates that methanol is replacing only the cordinated water from the hydrated ceric ion, $\mathrm{Ce(H_2O)_6}^{4+}$. Similarly the hydrolysis constants derived for 20 and 13°C, indicate the heat of hydrolysis to be 15.6 kcal. in agreement with Hardwick and Robertson's value of 15.3 kcal.

Summary

The oxidation of methyl alcohol by ceric perchlorate in perchloric acid solution was studied at 13, 20 and 26°C. The stoichiometry consisted of two ceric ions for the oxidation of one molecule of methanol. While the rate of disappearance of ceric ions directly depended on the concentration of ceric ions, the dependence on methanol concentration was such as to suggest a 'broken order':

$$\frac{-\mathrm{d\,Ce^{iv}}}{\mathrm{d}t}=\frac{k(\mathrm{Ce^{iv}})(\mathrm{MeOH})}{1+k'(\mathrm{MeOH})}$$

This rate also depended on the concentration of perchloric acid in such a way that at high acidity it became independent of it.

These data were explained on the basis of Duke's mechanism for 2, 3-butane diol-ceric perchlorate reaction, i. e. the oxidation of methanol by ceric ions proceeded via an intermediate complex between one Ce^{4+} ion and one methanol molecule. The formation of this complex was also proved independently by a spectrophotometric method. The kinetic data were further used to derive the true heat of formation of the methanol-cerate complex and the heat of hydrolysis of the ceric ions in aqueous perchloric acid.

Department of Chemistry
Osmania University
Hyderabad-7, India