340. *Oxidation of Ethanol by Ceric Perchlorate.*

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The oxidation of ethanol by ceric perchlorate proceeds *via* an intermediate complex between one Ce^{4+} ion and one ethanol molecule. This mechanism explains the kinetic data. The existence of the complex was proved independently by spectrophotometry.

THE kinetics and mechanism of oxidation of organic compounds by ceric perchlorate have been studied recently.[1,2] From their kinetic results on the oxidation of *meso*-2 : 3-butanediol (G) by ceric perchlorate, Duke and Bremer[1] suggested as a mechanism the intermediate formation of a complex or several complexes [*e.g.*, $CeG(H_2O)_4^{4+}$, $CeG_2(H_2O)_2^{4+}$] which decompose by unimolecular disproportionation.

As in much other kinetic work in solution, proof of the suggested mechanism was not sought by other than kinetic evidence, *e.g.*, by independently checking the existence and structure of the intermediate complex. This has been done in the present investigation.

The product of the reaction between ceric perchlorate and ethanol was acetaldehyde, the overall reaction being

$$2Ce^{4+} + EtOH \longrightarrow 2Ce^{3+} + Me{\cdot}CHO + 2H^+$$

This reaction could proceed by either termolecular collision or separate consecutive stages: (*a*) reduction of one ceric ion and production of a univalent radical or ion from the ethanol, and (*b*) the (quick) oxidation of the radical (ion) to acetaldehyde by a second ceric ion. This scheme, suggested by Duke and Bremer for *meso*-2 : 3-butanediol, was found to be correct and the first stage (*a*) was investigated in detail. Stage (*b*), not investigated, is outside the scope of this work. Stage (*a*) is preceded by a reversible formation of a complex between Ce^{4+} and ethanol which undergoes first-order decomposition

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[1] Duke and Bremer, *J. Amer. Chem. Soc.*, 1951, **73**, 5179.

[2] Hargraves and Sutcliffe, *Trans. Faraday Soc.*, 1955, **51**, 1105.

into Ce^{3+} and the radical (ion). This decomposition was found to be the rate-determining step and is followed by stage (*b*).

In many oxidations of organic substrates by quadrivalent cerium an intermediate complex can be clearly seen—the yellow colour deepens, becoming red in higher concentrations, and the absorption spectra, whose peak remains in the near ultraviolet, are extended further into the visible region. This phenomenon is especially noticeable with alcohols.

Ethanol reacts with ceric ions to produce a deep red colour;[3, 4] this is most intense with ceric perchlorate, less with the nitrate (owing to formation of the nitrato–ceric complexes) and negligible with the sulphate (owing to formation of the very stable sulphato–ceric complexes). Our object was to determine the role of this complex in the first stage of the oxidation.

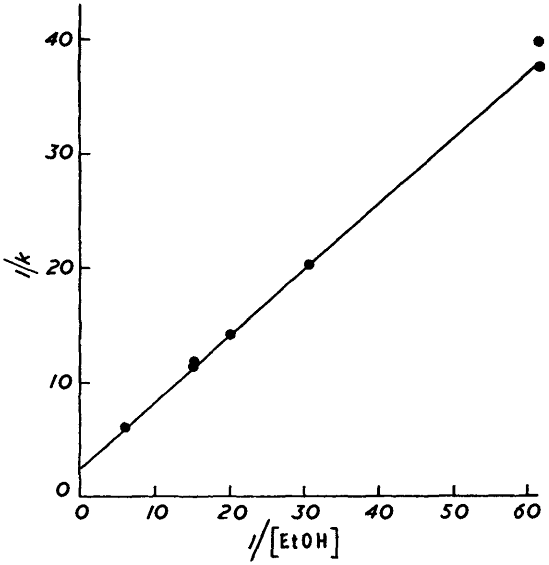

FIG. 1.

Kinetic Measurements.—At a constant pH ($[H^+] = 3{\cdot}2$N) and ionic strength, and a large excess of ethanol, the rate of the reaction was of the first order with respect to the total Ce^{IV} concentration: $-d[Ce^{IV}_{total}]/dt = k[Ce^{IV}_{total}]$.

The rate was measured either by titration of the remaining Ce^{IV}, or by measuring the optical density of the solution. Both methods gave similar results although the Ce^{IV} concentration was usually 5 times smaller in the spectrophotometric measurements. Since Beer's law is obeyed at a constant and large excess of ethanol, this agreement is to be expected.

The titrimetric method was finally abandoned and only the spectrophotometric method was used, because it allowed the use of lower cerium concentrations; this is desirable because (1) it minimizes the error due to acetaldehyde which is produced during the reaction and can be further oxidized by Ce^{IV} to acetic acid. Towards the end of the reaction this causes a slight increase of the overall rate and therefore a small deviation from the first-order graph. The rate of this side reaction at any fixed point in the main reaction is proportional to the second power of the initial Ce^{IV} concentration and therefore its effect on the overall rate decreases with decrease of the Ce^{IV} concentration; (2) the concentration of dimeric species such as $(Ce{-}O{-}Ce)^{6+}$ is negligible at $[H^+] = 3{\cdot}2$N and the lower concentration of cerium used in the spectrophotometric measurements[5] and thus the only Ce^{IV} species in solution are Ce^{4+} and $CeOH^{3+}$, their ratio being constant at the constant pH and ionic strength which was maintained in the measurement (see p. 1814).

From measurements at different ethanol concentrations it was found that the pseudo-first-order rate constant k obeys the law $1/k = 1/(k'[EtOH]) + 1/k''$. The plot of $1/k$ against $1/[EtOH]$ is a straight line (Fig. 1) which is interpreted as being identical with the well-known graph[1, 6] of $1/k = 1/(k_3K[EtOH]) + 1/k_3$.

This relation is derived by assuming the following scheme: Ce^{IV} reacts with ethanol

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[3] Meyers and Jacoby, *Z. anorg. Chem.*, 1901, **27**, 359.

[4] Duke and Smith, *Ind. Eng. Chem. Anal.*, 1940, **12**, 201.

[5] Hardwick and Robertson, *Canad. J. Chem.*, 1951, **29**, 818.

[6] Lineweaver and Burk, *J. Amer. Chem. Soc.*, 1934, **56**, 658.

and forms a reversible complex with it, consisting of one ethanol molecule and one ceric ion. The complex decomposes slowly into the products [stage (*a*)]

$$\mathrm{Ce^{IV}} + \mathrm{EtOH} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{complex} \xrightarrow{k_3} \text{products}$$

The equilibrium constant of the complex is $k_2/k_1 = K = [\text{complex}]/([\mathrm{Ce^{IV}}][\mathrm{EtOH}])$; k_3 is the first-order rate constant for the decomposition of the complex and k is the observed rate constant for the disappearance of the total $\mathrm{Ce^{IV}}$. From the graph K was found to be 4·3 ± 0·4 l. mole^{-1} and k_3 0·4 ± 0·04 min.$^{-1}$.

FIG. 2.

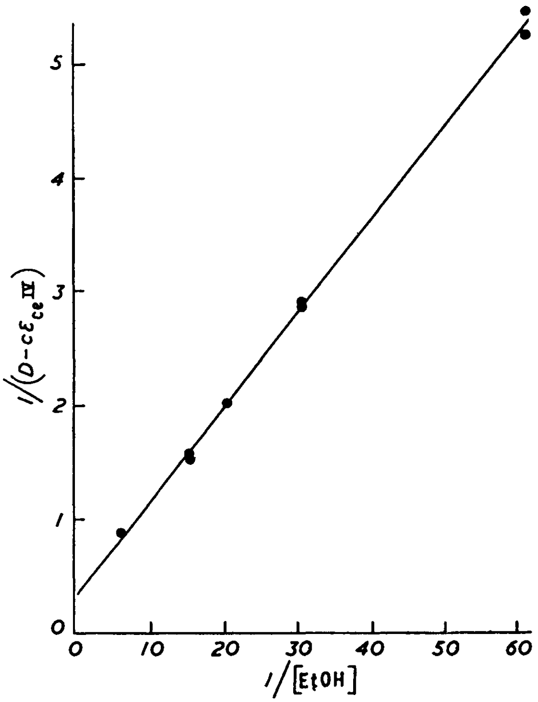

Fig. 1 shows that the proposed mechanism accords with the kinetic results, but that is insufficient proof of the mechanism because it is not necessarily the only mechanism conforming to them. If one could prove that a complex between ethanol and $\mathrm{Ce^{IV}}$ does exist, that its composition is $\mathrm{Ce_1,EtOH_1}$ and if, moreover, its equilibrium constant agreed with that calculated from Fig. 1, then the mechanism could be considered proved.

Job's method [7] gave an approximate ratio of 1 : 1 for the coloured complex Ce–ethanol but the experimental error was too great, owing to the fact that similar molar concentrations of ethanol and cerium must be used in this method; this caused a too quick decomposition at higher concentrations and a too small difference in light absorption at lower concentrations. Similar difficulties were encountered with other conventional methods. A special method was therefore developed, as follows.

If two species A and B, of which only A is coloured, react, producing a coloured complex (com) AB_n then the optical density D of the solution will be

$$D = c\varepsilon_{\text{com}} X + c\varepsilon_{\text{A}}(1 - X) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

ε_{A} and ε_{com} are the molar extinction coefficient of A and the complex respectively. c is the concentraction of $\mathrm{A_{total}}$ and X is the fraction of A combined in the complex. If B is in large excess so that $[\mathrm{B_{total}}] \sim [\mathrm{B_{free}}]$ and if the only reaction taking place is

$$\mathrm{A} + n\mathrm{B} \rightleftharpoons \mathrm{AB}_n$$

then
$$X/\{(1 - X)[\mathrm{B}]^n\} = K; \; X = K[\mathrm{B}]^n/(1 + K[\mathrm{B}]^n) \quad . \quad . \quad . \quad . \quad (2)$$

Insertion of the value of X in (1) gives

$$1/(D - c\varepsilon_{\text{A}}) = 1/\{Kc(\varepsilon_{\text{com}} - \varepsilon_{\text{A}})[\mathrm{B}]^n\} - 1/\{c(\varepsilon_{\text{com}} - \varepsilon_{\text{A}})\}$$

Thus the graph representing $1/(D - c\varepsilon_{\text{A}})$ as a function of $1/[\mathrm{B}]^n$ is a straight line if, and only if, the complex has the composition AB_n. In this case one can measure

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[7] Job, *Ann. Chim.* (*France*), 1928, **9**, 113; 1936, **6**, 97.

$1/\{c(\varepsilon_{com} - \varepsilon_A)\}$ and $1/K$ from the slope of the graph and its point of intersection with the y axis. This method is practicable only for $n = 1$. Thus the graph of $1/(D - c\varepsilon_A)$ against $1/[B]$ will be a straight line if, and only if, the complex is A_1B_1.* In the experiments at 400 mμ it was found that a straight line is indeed obtained (Fig. 2) and K was found to be $4{\cdot}3 \pm 0{\cdot}7$ l. mole^{-1}, in excellent agreement with the value based on the kinetic data ($4{\cdot}3 \pm 0{\cdot}4$).

Thus the suggested mechanism is considered to be proved.

pH *Dependence.*—Ceric ions in perchloric acid solution consist of the monomeric species Ce^{4+}, $CeOH^{3+}$, etc., and of dimeric species such as $(Ce{-}O{-}Ce)^{6+}$. In low acidity (pH > 0·8) polymerisation proceeds beyond this stage and irreversible colloidal polymers are formed.[8] At higher acidity the hydrolysis constants derived by Hardwick and Robertson [5] are applicable.

Using their data and converting them to 20° we obtained $[CeOH^{3+}][H^+]/[Ce^{4+}] = 3{\cdot}4$ mole l.$^{-1}$ and $[Ce{\cdot}O{\cdot}Ce^{6+}]/[CeOH^{3+}]^2 = 24{\cdot}5$ l. mole^{-1}. At $[H^+] = 3{\cdot}2$N, $[CeOH^{3+}][/Ce^{4+}] = 1{\cdot}06$. At a Ce^{VI} concentration of 0·0035N the dimer $(Ce{-}O{-}Ce)^{6+}$ is only about 2% of the total Ce^{IV} and therefore can be neglected in approximate calculations. The only species existing in quantity are Ce^{4+} and $CeOH^{3+}$ and therefore $[Ce^{4+}]/[Ce^{IV}] = 0{\cdot}49$ where $[Ce^{IV}]$ is the free quadrivalent cerium (not combined with ethanol).

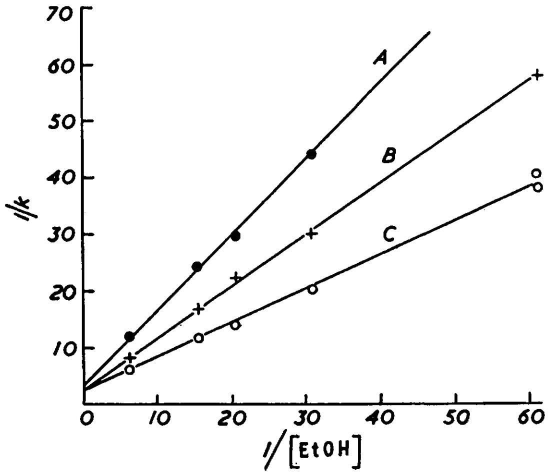

FIG. 3. $[H^+] = A$, 0·79N; B, 1·73N; C, 3·20N.

If the complex is between Ce^{4+} and ethanol then K cannot be a real equilibrium constant, but should vary with the pH. By inserting the value of $[Ce^{4+}]$, from the last equation, we can find the real equilibrium constant $\bar{K}$ which is $\bar{K} = [com]/([Ce^{4+}][EtOH]) = 8{\cdot}8 \pm 0{\cdot}8$ l. mole^{-1}. Although K is expected to decrease with decreasing H^+ concentration $\bar{K}$ should remain constant.

In two series of experiments (Fig. 3), K was found to decrease as expected (within experimental error).

$[H^+]$	$K_{calc.}$	K_{found}	$\bar{K}_{calc.}$	$\bar{K}_{found}$
3·2	—	$4{\cdot}3 \pm 0{\cdot}4$	8·8	—
1·73	$2{\cdot}9 \pm 0{\cdot}3$	$2{\cdot}7 \pm 0{\cdot}4$	8·8	$8{\cdot}1 \pm 1{\cdot}1$
0·79	$1{\cdot}7 \pm 0{\cdot}2$	$1{\cdot}8 \pm 0{\cdot}4$	8·8	$9{\cdot}5 \pm 2$

The pH dependence confirms the assumption that only Ce^{4+} and not its hydrolysis products take part in the complex formation. The assumption is further supported by

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* This method was used by Benesi and Hildebrand [9] for the special case where $\varepsilon_A = 0$.

[8] Ardon and Stein, *J.*, 1956, 104.

[9] Benesi and Hildebrand, *J. Amer. Chem. Soc.*, 1949, **71**, 2703.

the fact that the value of k_3 is the same at different H^+ concentrations. This proves that there is only one (and the same) complex which decomposes, as described. It should be remembered that in these experiments the ionic strength was not kept constant and therefore a slight deviation from the calculated value is expected, but this does not exceed the experimental error. On the other hand, an attempt to keep the ionic strength constant by substituting Na^+ for H^+ causes a very large positive deviation because Na^+ is much more hydrated[10] than H^+ and at a concentration of 3N in Na^+ it causes a drastic decrease in the activity of water. The concentration of water enters the equilibrium constant because the reaction is in fact

$$Ce(H_2O)_6^{4+} + EtOH \rightleftharpoons Ce(H_2O)_5,EtOH^{4+} + H_2O$$

and therefore a much higher concentration of the complex at high salt concentrations is expected.

Higher complexes such as $Ce(EtOH)_2^{4+}$, $Ce(EtOH)_3^{4+}$, etc., are very likely to exist in higher ethanol concentrations than those used here, but the results point to the fact that no appreciable amounts are formed with the ethanol concentrations used.

EXPERIMENTAL

Ceric Perchlorate Solution.—Ceric hydroxide, $Ce(OH)_4$, was precipitated by ammonium hydroxide from a solution of ceric ammonium nitrate, and rinsed with water until all trace of ammonia was removed.

The hydroxide was reduced by hydrogen peroxide in perchloric acid and an acidified solution of cerous perchlorate resulted from which ceric perchlorate was prepared by electrolytic oxidation; the resulting solution was 0·366M in total cerium and 0·358—0·350N in quadrivalent cerium. The concentration of perchloric acid was 3·2N.

Ethanol was redistilled and its concentration was found to be 16·55M (from the density). Triply distilled water was used throughout. All reagents were " AnalaR."

Acetaldehyde was determined gravimetrically as the 2 : 4-dinitrophenylhydrazone. The yield was 90%.

Spectrophotometric measurements were made with a Beckman B Spectrophotometer at 400 mμ. A two compartment cell (similar to a Thunberg tube) was constructed by addition of a side compartment to a 1 cm. Beckman Pyrex cell, which permits the separate storage of two liquids which can be mixed by inverting the cell.

1 ml. of the ceric solution (diluted 1 : 10 with 3·2N-perchloric acid) was placed in one compartment, and a measured amount of diluted ethanol in the other. Enough 4·7N-perchloric acid and water were added to make the final concentration of perchloric acid 3·2N and the final volume 10 ml.

After being kept for 20 min. in a thermostat at 20° ± 0·05° the liquids were mixed and at specific intervals (1—10 min.) the cell was removed and dried and the optical density was measured. The measurement took about 10 sec. and the temperature variation due to removal from the thermostat did not exceed 0·1°.

The measurements for determination of the complex structure were made in the same way, but the cell was dried before mixing; in this way the time of measurement was reduced to 6 sec. The small error (less than 2%) due to decomposition during these 6 sec. was calculated from the known value of the rates of decomposition, and the results were adjusted accordingly.

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[10] Cf. International Critical Tables, Vol. 6, p. 311; Glasstone, " Textbook of Physical Chemistry," Macmillan, London, 1951, p. 921.