Oxidation of Alcohols by Cerium(IV). II. Oxidation of Methanol by Ceric Sulfate

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Benrath and Ruland[1] were the earliest to investigate the oxidizing action of ceric sulfate on several substances, while Lejune[2] studied the oxidizability of alcohols, aldehydes and ketones by potassium permanganate and potassium dichromate. Later Willard and Young[3] observed the unreactivity of formic and acetic acids towards ceric sulfate and complicated kinetics and stoichiometry in the case of tartaric, malonic and other acids. Ross and Swain[4] tried to apply the principle of the concentration cells to kinetic studies on the oxidation of oxalic acid by ceric sulfate. The work of Shorter and Hinshelwood[5] concerned the oxidation of acetone[6] by ceric sulfate in dilute sulfuric acid. They assumed direct reaction between trisulfato-hydroxy cerate ion $\{H_2CeOH(SO_4)_3\}^-$ with enolic form of acetone. Hargreaves and Sutcliffe[7], using rather high concentrations of sulfuric acid, found the rate of oxidation of formaldehyde to depend on the cubic exponent of sulfuric acid concentration, indicating tetra-sulfate ceric acid $H_4Ce\cdot(SO_4)_4$ to be the reactive species. Dodson and Black[8] favored the existence of the trisulfato cerate ions $Ce(SO_4)_3{}^{2-}$ in soulution and assumed the main reductant to be the bioxalate ion $HC_2O_4{}^-$. Shao Minchzhou and Gorbachev[9]

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1) A. Benrath and K. Ruland, *Z. anorg. Chem.*, **114**, 267 (1920).
2) G. Lejune, *Compt. rend.*, **181**, 694 (1926).
3) H. H. Willard and P. Young, *J. Am. Chem. Soc.*, **52**, 132 (1930).
4) S. D. Ross and C. G. Swain, ibid., **69**, 1325 (1947).
5) J. Shorter and C. N. Hinshelwood, *J. Chem. Soc.*, **1950**, 3276,
6) See also J. Shorter, ibid., **1950**, 3425.
7) G. Hargreaves and L. H. Sutcliffe, *Trans. Faraday Soc.*, **51**, 1105 (1955).
8) V. H. Dodson and A. H. Black, *J. Am. Chem. Soc.*, **79**, 3657 (1957).
9) S. Minchzhou and S. V. Gorbachev, *Zhur. Fiz. Khim.*, **32**, 635 (1958).

studied the oxidation of methanol, ethanol, isopropanol, *n*- and iso-butanol and benzyl alcohol with potassium permanganate and ceric sulfate and activation energy of these reactions was correlated with dipole moments of the alcohols. Mino, Kaizerman and Rasmussen[10] studied the oxidation of pinacol by ceric sulfate and found no evidence of complexing between the reactants. They also noticed that in presence of acrylamide the primary radicals are captured by it. Krishna and Tewari[11] studied the oxidation of mandelic, *dl*-malic and lactic acids by ceric sulfate.

The present work concerns the study of the kinetics of the oxidation of methanol by ceric sulfate and activation data for the oxidation of methanol, ethanol and *n*-propanol.

Experimental Results

The ceric ammonium sulfate was of Merck's analar. It was dissolved in standardized sulfuric acid of highest purity and was assayed with ferrous ammonium sulfate. Other experimental details remain the same as given in Part I. Ceric sulfate solutions are much more stable as compared to ceric perchlorate. They do not decompose or undergo dimerization. Hence the rates could be followed in ordinary daylight.

The stoichiometry of reaction proves to be 2 ceric sulfate for each methanol molecule, the same as found with ceric perchlorate-methanol reaction.

Effect of Added Bisulfate Ion on Methanol-Ceric Perchlorate Reaction.—Addition of potassium hydrogen sulfate causes large retardation in the oxidation of methanol by ceric perchlorate. Thus using 3.55×10^{-3} M ceric perchlorate and 0.15 M methanol at 20°C, we get the data of Table I.

TABLE I. EFFECT OF ADDED BISULFATE IONS

$KHSO_4$ added g.	0	0.10	0.20	0.30	0.40	0.50
Apparent rate constant $x\times10^2$ min^{-1}	8.60	5.07	3.80	3.38	3.03	2.82

Methanol-Ceric Sulfate Reaction in Perchloric Acid.—The log-time plots showed the order to be one with respect to cerium(IV). Using differential method, the value of the exponent

$$n=\frac{\log (k_2/k_1)}{\log (C_2/C_1)}$$

was found to be one, where k_2 and k_1 are first order constants with methanol concentrations C_2 and C_1 in identical conditions.

The effect of perchloric acid was similar to ceric perchlorate-methanol reaction and the reciprocals of rates versus reciprocals of acid concentration, gave a straight line. Further the sodium perchlorate added results in a positive salt effect. But the search for complex formation led to negative result as the plot of $1/k'$ against 1/(MeOH) gave a straight line without an intercept (similar to Fig. 4). Hence it may be concluded that methanol and ceric sulfate in perchloric acid react without the prior formation of a complex.

Methanol-Ceric Sulfate Reaction in Sulfuric Acid.—The rate of oxidation depends directly on the concentrations of ceric sulfate and methanol. The plots of log titre value against time gave a straight line. The first order

TABLE II. DEPENDENCE OF OXIDATION ON METHANOL

Ceric sulfate 4.2×10^{-3} M, sulfuric acid 1.0 M, temp. 55°C

MeOH M	$k\times10^3$ min^{-1}	rel. k	rel. (MeOH)	log rel. k	log rel. (MeOH)
1.00	5.68	1.00	1.00	0.000	0.000
1.50	8.15	1.46	1.50	0.158	0.176
2.00	10.45	1.84	2.00	0.265	0.301
2.50	13.51	2.38	2.50	0.376	0.398
3.00	16.67	2.94	3.00	0.468	0.477
4.00	21.68	3.81	4.00	0.582	0.602

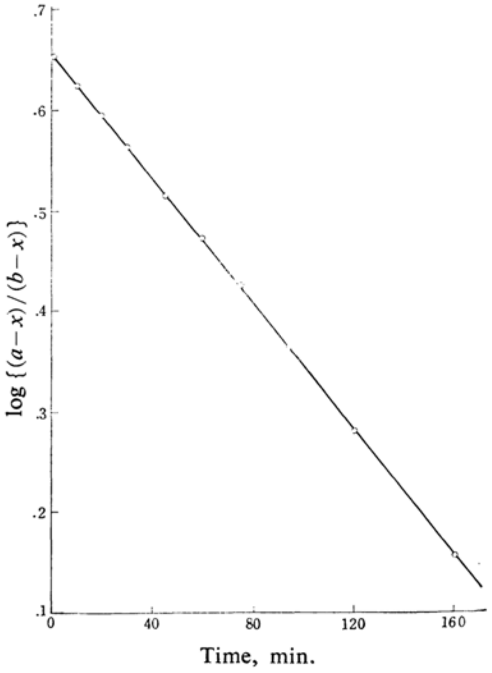

Fig. 1. Verification of order 2.

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

[11] B. Krishna and K. C. Tewari, *J. Chem. Soc.*, **1961**, 3097.

character with respect to ceric sulfate continues till half of ceric sulfate is consumed, after which the rate falls off. The plot of log rel. (methanol) versus log rel. (first order constant), gave a straight line with a slope of unity. These data are contained in Table II. Hence the dependence of oxidation on methanol is of first order and the overall order of this reaction is two. This was varified by plotting $\log\{(a-x)/(b-x)\}$ against time (Fig. 1), using a = (ceric sulfate) = 6.75×10^{-3} M, b = (methanol) = 1.5 M and (sulfuric acid) = 1.0 M at temperature 55°C.

Effect of Sulfuric Acid and Ionic Strength.—Keeping the ionic strength constant at 2.53 M at 55°C the solutions containing 1.5 M methanol and 4.2×10^{-3} M ceric sulfate were made 0.5 M to 2.0 M with respect to surfuric acid. The plot of initial rate against molarity of sulfuric acid is shown in Fig. 2. This shows direct dependence of rate on the concentration of the acid. But when the ionic strength is not maintained constant, the rate decreases directly with increase of sulfuric acid concentration. Besides, when the sulfuric acid concentration is maintained constant the plot of log of initial rate against (ionic strength)$^{1/2}$ shows a negative salt effect (Fig. 3).

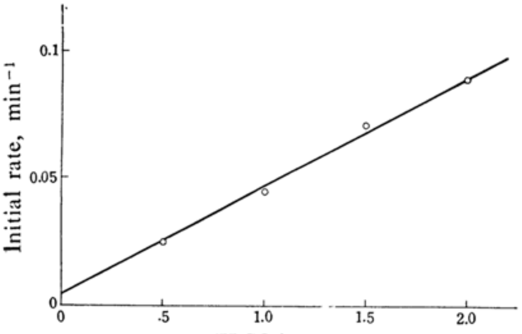

Fig. 2. Effect of acidity.

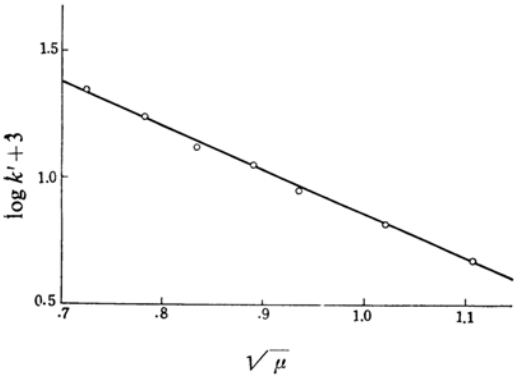

Fig. 3. Effect of ionic strength.

Effect of Temperature.—Using mixtures of 2.0 M methanol, 1.5 M sulfuric acid and 4.2×10^{-3} M ceric sulfate, the first order rate constants were determined at different temperatures and are given in Table III. The Arrhenius plot gives the value of 26300 cal. mol^{-1} for the activation energy.

TABLE III. VARIATION OF RATE CONSTANTS WITH TEMPERATURE

Temp. °K	First order rate constant $\times10^3$ min^{-1} (each is a mean of 3 expts.)	Mean k $\times10^3$ min^{-1}
313.2	2.50, 2.32, 2.61	2.48
318.2	4.64, 4.39, 4.48	4.50
323.2	8.68, 8.47, 8.27	8.47
328.2	14.15, 15.76, 14.76	14.88
333.2	32.53, 32.24, 32.20	32.32
338.2	56.56, 57.01, 55.51	56.36

Search for Complex Formation.—The plot of $1/k'$ against 1/(MeOH) (Fig. 4) is a straight line passing through the origin. Similarly the plot of $1/(D-D')$ against 1/(MeOH) is a straight line passing through the origin. Both facts show that the complex is not formed during oxidation.

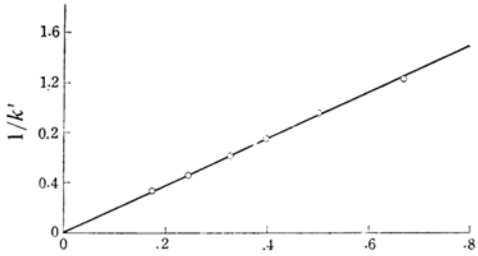

Fig. 4. Search for complex formation.

Discussion

The oxidation of methanol by ceric sulfate exhibits the same stoichiometry as the reaction of alcohols with ceric perchlorate, indicating that this also consists of two stages—the first being the slow reaction:

$$\mathrm{Ce^{iv}} + \mathrm{CH_3OH} \rightarrow \mathrm{Ce^{iii}} + \mathrm{CH_3\dot{O}} + \mathrm{H^+} \quad (1)$$

followed by the very fast step:

$$\mathrm{Ce^{iv}} + \mathrm{CH_3\dot{O}} \rightarrow \mathrm{Ce^{iii}} + \mathrm{HCHO} + \mathrm{H^+} \quad (2)$$

But the fact that in sulfuric acid medium, oxidation of alcohols does not involve the formation of a complex implies a difference between the mode of oxidation in the two media. This might be due to the difference in the state of Ce^{iv} in the two media.

The stability of ceric sulfate solutions compared to easy decomposition of ceric perchlorate and the fact that addition of alcohol to ceric sulfate does not change its color[12] are suggestive of covalent bonding between cerium(IV) and sulfate. While ion migration studies by Jones and Soper[13] and spectrophotometric studies by Hardwick and Robertson[14] support this, they do not agree about the species existing in solution[15]. Similarly, as shown in the introduction, different authors have assumed the existence of diffenent complexes to explain their kinetic data. It has to be admitted that in aqueous sulfuric acid solutions of ceric sulfate, several complexes can exist depending on the concentration of ceric sulfate and sulfurid acid such as

$$\{Ce(SO_4)\}^{2+},\ \{Ce(OH)SO_4\}^{1+},\ \{Ce(SO_4)_2\},$$
$$\{Ce(SO_4)_3\}^{2-},\ \{HCe(SO_4)_3\}^{1-},$$
$$\{H_2Ce(SO_4)_4\}^{2-} \text{ and } \{Ce(SO_4)_4\}^{4-}$$

The choice of the right species is difficult. But our observation that the rate of oxidation of methanol by ceric perchlorate is retarded by added sulfuric acid and also the observation that the oxidation of methanol by ceric sulfate decreases on the addition of sulfuric acid point to the fact that the relative species should be the covalent by bond ceric sulfate $Ce(SO_4)_2$.

Mechanism of Waters.—Admitting that the reactive participants are the neutral ceric sulfate and methanol, the course of reaction may be assumed to be analogous to that proposed by Waters and Levesley[16] for the oxidation of α-hydroxy acids by manganese pyrophosphate. Earlier this mechanism was adopted by Krishna and Tiwari[11] to explain the kinetics of the oxidation of mandelic and *dl*-malic and lactic acids.

Hence we assumed that ceric sulfate and methanol react to form a transition complex which decomposes to produce a free radical, a hydrogen ion and cerous sulfate complex. The free radical then picks up another ceric sulfate (as in the case of ceric perchlorate-methanol reaction) and quickly produces the final products of reaction:

$$Ce(SO_4)_2 + CH_3OH \rightarrow \underset{\text{transition state}}{Ce(SO_4)_2\cdots\cdots CH_3OH}$$
$$\rightarrow Ce^{iii}(SO_4)_2 + H^+ + CH_3\dot{O} \qquad (3)$$

$$Ce(SO_4)_2 + CH_3\dot{O}$$
$$\xrightarrow{\text{very fast}} Ce^{III}(SO_4)_2 + H^+\ HCHO \qquad (4)$$

The retarding action of bisulfate ions at constant acidity can be explained as due to the removal of ceric sulfate by the reaction

$$Ce(SO_4)_2 + HSO_4^- \rightleftharpoons HCe(SO_4)_3^- \qquad (5)$$

while the accelerating effect of hydrogen ions at constant ionic strength might be due to the reactions:

$$Ce(SO_4)_2 \rightleftharpoons Ce(SO_4)^{2+} + SO_4^{2-} \qquad (6)$$
$$Ce(SO_4)^{2+} + H_2O \rightleftharpoons Ce(OH)SO_4^- + H^+$$

According to reaction 3, the rate of disappearance of ceric sulfate

$$\frac{-d(Ce(SO_4)_2)}{dt} = k''\,[Ce(SO_4)_2]\,[CH_3OH] \qquad (a)$$

and the rate is first order with respect to both reagents and the overall order is 2. Hence the bimolecular constant can be calculated by

$$k'' = \frac{2.303}{t(a-x)} \log \frac{b(a-x)}{a(b-x)} \qquad (b)$$

where $a>b$ and x is the quantity of cerium(IV) disappearing in the time interval t.

From Eq. 5,

$$[C(SO_4)_2] = \frac{[HCe(SO_4)_3^-]}{K[HSO_4^-]}$$
$$\frac{-d\ (Ce(SO_4)_2)}{dt} = \frac{k''\,[HCe(SO_4)_3^-]\,[MeOH]}{K[HSO_4^-]} \qquad (c)$$

Assuming that ceric sulfate in sulfuric acid exists largely as $HCe(SO_4)_3^-$, the concentration of the latter is proportional to that of cerium(IV) and $HSO_4^- \propto H_2SO_4$, we arrive at the rate equation:

$$\frac{-d\,Ce^{iv}}{dt} = \frac{k'\,[MeOH]\,[Ce^{iv}]}{[H_2SO_4]} \qquad (d)$$

Evidence for the Proposed Mechanism.—The proposed mechanism is also supported by the behavior of methanol-ceric sulfate in perchloric acid medium. The reaction between methanol and ceric sulfate is very fast due to the absence of the bisulfate ions which slow down the reaction by removing ceric sulfate in the form of the complex ion $HCe(SO_4)_3^-$. Further the hydrogen ions of the perchloric acid stop the hydrolysis and degradation of the ceric sulfate (as shown in Eqs. 6 and 7).

According to Hinshelwood and Fairclough[17]

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[12] F. R. Duke and G. F. Smith, *Ind. Eng. Chem. Anal. ed.*, **12**, 201 (1940).

[13] E. G. Jones and F. G. Soper, *J. Chem. Soc.*, **1930**, 802.

[14] T. J. Hardwick and E. Robertson, *Can. J. Chem.*, **29**, 828 (1951).

[15] For example: W. Moore and R. C. Anderson, *J. Am. Chem. Soc.*, **67**, 167 (1945), disagree with Ref. 14.

[16] W. A. Waters and P. Levesley, *J. Chem. Soc.*, **1955**, 217.

[17] C. N. Hinshelwood and R. A. Fairclough, *J. Chem. Soc.*, **1937**, 538, 1573.

Table IV. Relation between $(1/E)^{1/2}$ and log PZ for oxidation of alcohols by Ce^{iv}

	Reaction system	Medium	E, cal. mol^{-1}	$\sqrt{1/E}\times 10^3$	log PZ
1	Methanol-ceric sulfate	Sulfuric acid	21850	6.76	10.74
2	Ethanol-ceric sulfate	Sulfuric acid	18800	7.59	9.10
3	*n*-Propanol-ceric sulfate	Sulfuric acid	13860	8.50	6.32
4	Methanol-ceric sulfate	Perchloric acid	12210	9.05	6.08

Data obtained with $Ce^{iv}=3.55\times 10^{-3}$ M, $H_2SO_4=1.0$ M and rate constants derived from Eq. d

in a series of related reactions, the relation between $(1/E)^{1/2}$ and log PZ should be linear. In Table IV are recorded the values of the activation energy E, the square root of its reciprocal $(1/E)^{1/2}$ and the logarithm of the product of steric fator P and the collision number Z for the reactions of the three alcohols, methanol, ethanol and *n*-propanol with ceric sulfate as obtained in the present study:

Figure 5 is the graphical representation of log PZ against $(1/E)^{1/2}$. The four systems lie on a smooth line with a slope -2.16×10^3. This value of slope, according to Hinshelwood, is a characteristic of many bimolecular reactions.

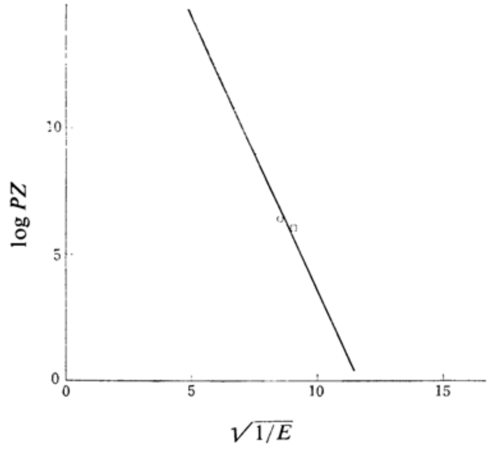

Fig. 5. Relation between $(1/E)^{1/2}$ and log PZ.

Summary

The oxidation of methanol by ceric sulfate in sulfuric acid solutions was studied in the temperature range 40∼70°C. The rate of oxidation depended directly on the concentration of cerium(IV) and methanol. At constant ionic strength the rate was directly dependent on the concentration of sulfuric acid. But when the ionic strength is not maintained, the rate changes inversely with sulfuric acid. At constant acid concentration, a negative salt effect is observed. The reaction occurs without the intermediate formation of a complex. The activation energy was derived to be 26300 cal. mol^{-1}. It has been shown that the mechanism of Waters for the oxidation of α-hydroxyacids by manganese pyrophosphate can be used to explain the present data.

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