

OXIDATION STUDIES

IV. Kinetics of Oxidation of HCHO and Some Alcohols by Ceric Salts in HNO₃ Medium

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ABSTRACT

The results on the kinetics of oxidation of HCHO and some alcohols, viz., *n*-propanol, allyl alcohol, cyclohexanol and benzyl alcohol by ceric nitrate in nitric acid medium in the temperature range of 10–35° C. are presented. The active form of Ce⁴⁺ during the oxidation of the above organic substrates was assumed to be the neutral Ce(NO₃)₄. The mechanism of oxidation and thermodynamic parameters for the above compounds are also given.

INTRODUCTION

It is now well recognised that the species involving ceric ions differ in types and activity depending upon the medium being H₂SO₄ or HClO₄ or HNO₃. Kinetic and mechanistic studies on the oxidation of various organic substrates by ceric salts were carried out extensively in H₂SO₄ medium,¹⁻⁹ to somewhat lesser extent in HClO₄¹⁰⁻¹⁵ and to the least extent in HNO₃ medium.¹⁶⁻¹⁹ An excellent review of oxidation of various types of substrates by Ce⁴⁺ has been given by Richardson.²⁰ Ceric ion oxidation of primary alcohols lead to the corresponding aldehydes¹³ while those of secondary¹⁹ and tertiary alcohols²⁰ lead to the corresponding ketones. As a result of extensive studies in H₂SO₄ and HClO₄ media the mechanism suggested involved the formation of Ce⁴⁺-alcohol complex followed by unimolecular decomposition of the latter in a rate determining step to yield the products. The crucial issue regarding the nature of decomposition involving the rupture of O-H or α-C-H bond in alcohols was sought to be resolved by the oxidation of deuterated cyclo-hexanol (deuterated

at α -C-H and O-H position separately) by Littler and Waters²¹ and Littler.²² On the basis of the low value of $k_{\text{CH}}/k_{\text{CD}} \approx 1.9$ for α -C-D alcohol during oxidation by ceric sulphate²² and $k_{\text{OH}}/k_{\text{OD}} \approx 1.0$ for O-D alcohol, it was suggested that the α C-H fission might be preponderant, though a concerted mechanism (*cf.* Littler²³) involving both C-H and O-H fissions could not be ruled out. Shorter³ studied the oxidation of acetaldehyde by ceric sulphate in sulphuric acid and concluded that the active form of aldehyde was not enol, for, the oxidation rate was found to be faster than would be expected by an enol mechanism. Hargreaves and Sutcliffe's⁴ studies on the oxidation of HCHO by ceric salts in H_2SO_4 and HClO_4 media have lead to the conclusion that no Ce^{4+} -HCHO complex formation was involved at low concentrations of HCHO. Studies on the oxidation of secondary alcohols, iso-propanol and secondary butanol by ceric nitrate in nitric acid medium by Sethuram and Muhammad¹⁹ showed that neutral ceric nitrate molecule $\text{Ce}(\text{NO}_3)_4$ was the active species and that H^+ had no effect on the rate. Results of oxidation of HCHO and alcohols, *viz.*, *n*-propanol, allyl alcohol, benzyl alcohol and cyclohexanol by ceric nitrate in nitric acid medium (1–3 M) at 10–35° C. are presented and discussed in this paper.

EXPERIMENTAL.

Formaldehyde solutions (2.0 M) were prepared by dissolving HCHO gas (obtained by heating paraformaldehyde) and estimated by the bisulphite method.²⁴ The alcohols, *n*-propanol (E. Merck), allyl alcohol (May and Baker), benzyl alcohol (B.D.H.—A.R.), cyclohexanol (May and Baker) were distilled before use and the middle fractions were used for kinetic experiments. A three-necked quickfit flask (500 ml.) provided with a mercury seal stirrer in the middle neck, a gas inlet tube in the first neck to pass purified nitrogen gas, a gas outlet *cum*-aliquot withdrawing arrangements in the third neck was the reaction vessel for conducting oxidation studies. The systems (i) substrates ($[\text{HCHO}] = 0.05 \text{ M}$ or $[\text{alcohols}] = 0.5 \text{ M}$) and (ii) ceric nitrate (7×10^{-3} in 1.0 M HNO_3) were thermostated at 20° C. separately; 50 ml. of (ii) was added to 50 ml. of (i) and the rate of oxidation was followed by pipetting out 10 ml. of aliquots at intervals of 5 mts., quenching the latter in 10 ml. of standard ferrous ammonium sulphate (0.01 M), back titrating the excess of the latter by standard ceric sulphate using methyl red as indicator and estimating $[\text{Ce}^{4+}]$ that reacted. Rates of ceric ion disappearance, $-\text{R}_{\text{Ce}^{4+}}$, were computed with varying concentrations of $[\text{Ce}^{4+}]$, $[\text{Substrate}]$, $[\text{H}^+]$ at constant ionic strength

($\mu = 3.5$ M) and $[\text{NO}_3^-]$ at constant $[\text{H}^+]$. Reactions were usually conducted for 25 to 30 mts. in the case of HCHO and 45–60 mts. in the case of alcohols and for 60–70% conversion of ceric ion. For studies on ceric-alcohol complex formation, optical methods due to Ardon¹³ and others¹⁹ were followed.

RESULTS AND DISCUSSION

1. Formaldehyde and Ce^{4+}

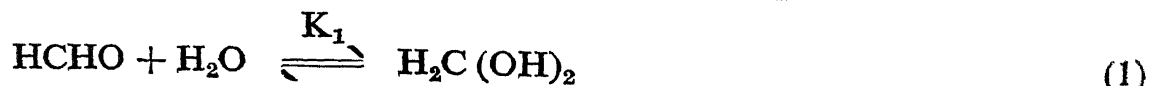
(i) *Some general features.*—The system HCHO– Ce^{4+} initiated vinyl polymerisation²⁵ thereby indicating that free radical intermediates were involved. Ceric salts are known to form complexes with aliphatic alcohols and other substrates both in HClO_4 and HNO_3 media.³⁰ As per our experiments addition of HCHO (0.05 M) to ceric salt solution (3×10^{-3} M) in 1.0 M nitric acid did not produce any intensification of the colour which indicated absence of complex formation.

(ii) *Orders of reactants.*—Under conditions of $[\text{HCHO}] > [\text{Ce}^{4+}]$ ($[\text{Ce}^{4+}] = 3 \times 10^{-3}$ M, $[\text{HCHO}] = 0.033$ M); $[\text{H}^+] = 1.0$ M, $t = 20^\circ$ C. and $\mu = 1.03$ M, the order with respect to $[\text{Ce}^{4+}]$ was unity (Fig. 1 *a*). The plot of log. of the slopes of plots in Fig. 1 *a* vs. log $[\text{HCHO}]$ was linear with a slope of unity (Fig. 1 *b*) and hence order with respect to $[\text{HCHO}]$ was also unity.

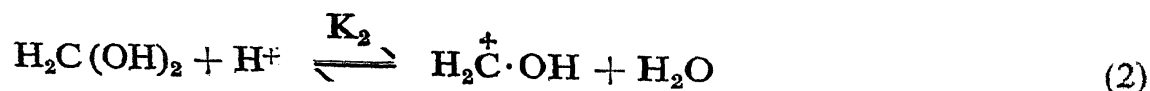
(iii) *Effect of $[\text{H}^+]$.*—Increase of $[\text{H}^+]$ from 0.5 M ($k_{\text{obs.}} = 8.7 \times 10^{-2}$ min.⁻¹) to 3.5 M ($k_{\text{obs.}} = 2.7 \times 10^{-2}$ min.⁻¹) at constant ionic strength 3.53 M decreased the rate by about 55%.

(iv) *Effect of added $[\text{NO}_3^-]$.*—The rate decreased by 70% when $[\text{NO}_3^-]$ was increased from 1.0 ($k_{\text{obs.}} = 14.4 \times 10^{-2}$ min.⁻¹) to 3.5 M ($k_{\text{obs.}} = 3.8 \times 10^{-2}$ min.⁻¹) at constant $[\text{H}^+]$.

(v) *Mechanism.*—In the studies involving HCHO, equilibria (1) and (2) exist: Formaldehyde exists as a diol,²⁶ $\text{H}_2\text{C}(\text{OH})_2$:



And the diol is involved in equilibrium²⁷ with H_2COH^+



Our foregoing experimental results may be satisfactorily explained by a mechanism involving reactions (3) and (4) below:

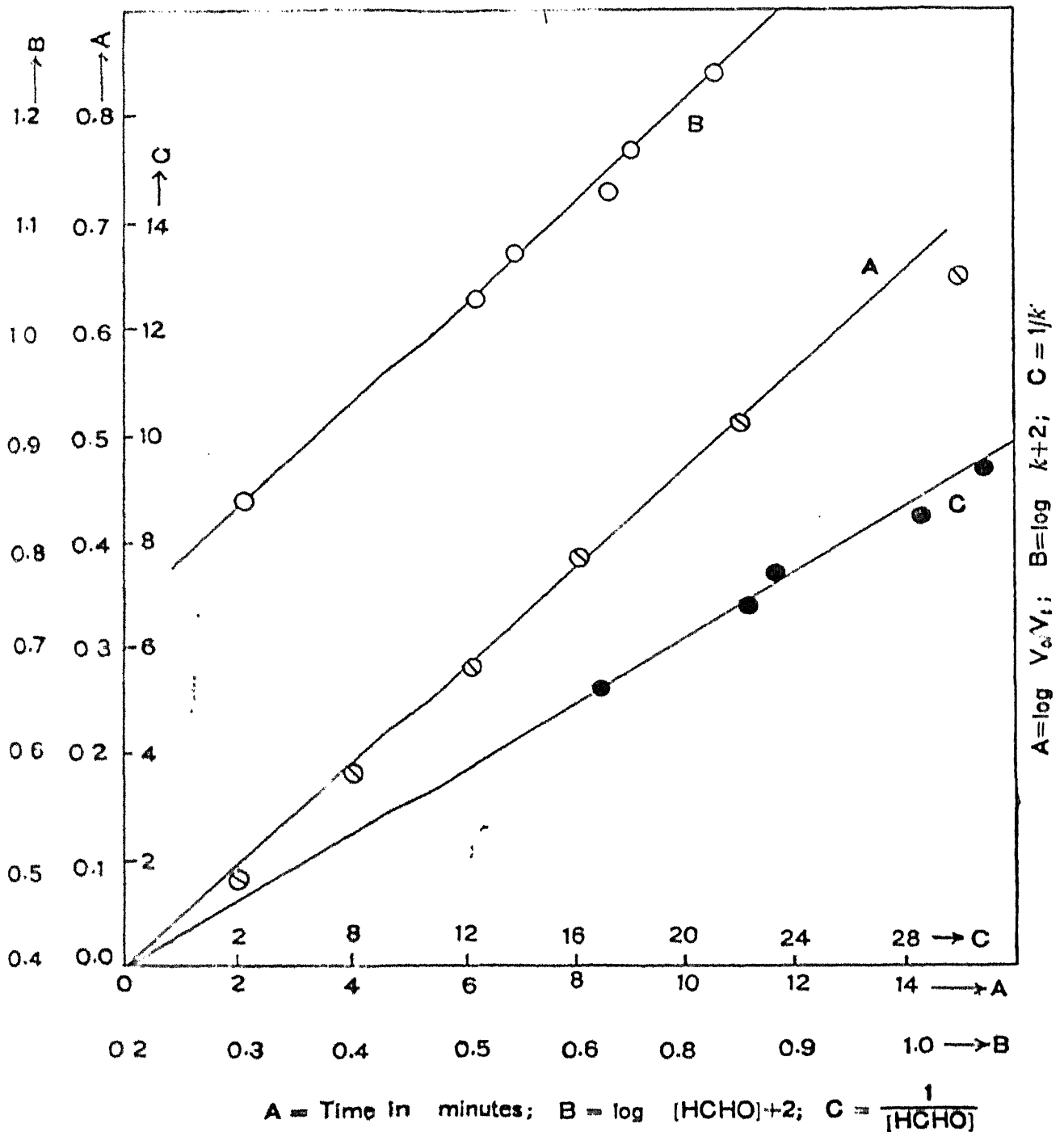
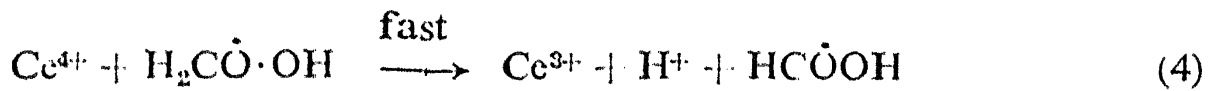
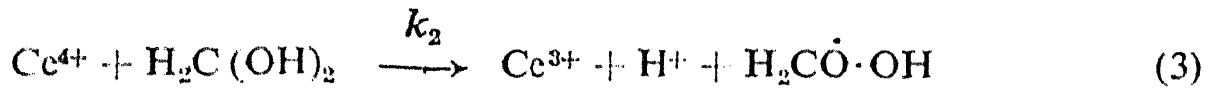


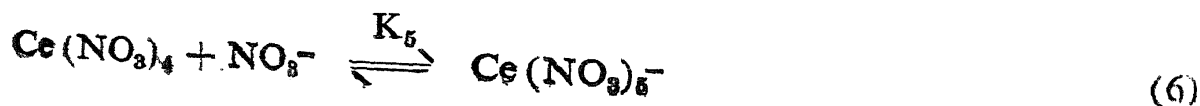
FIG. 1. (a) Order of $[\text{Ce}^{4+}]$ in $-d\text{Ce}^{4+}/dt$ with HCHO as substrate in nitric acid medium. Plot of $\log V_0/V_t$ vs. time in minutes. V_0 initial titre value. V titre value at time t . $[\text{Ce}^{4+}] = 2.65 \times 10^{-3} \text{ M}$; $[\text{HNO}_3] = 1.0 \text{ M}$; $[\text{HCHO}] = 0.0324 \text{ M}$; Temperature = 20°C . (b) Order of $[\text{HCHO}]$. Plot of $\log k' + 2$ vs. $\log [\text{HCHO}] + 2$. $[\text{Ce}^{4+}] = 2.65 \times 10^{-3} \text{ M}$; Temperature = 20°C ; $[\text{HNO}_3] = 1.0 \text{ M}$; $[\text{HCHO}] = 0.03$ to 0.06 M . (c) Search for the complex. Plot of $1/k'$ vs. $1/[\text{HCHO}]$. Conditions same as in (b).

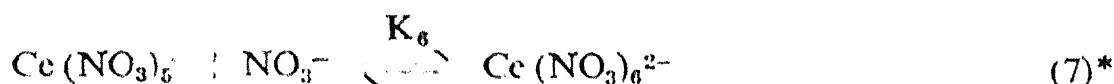
The decrease in rate with increase of H^+ may be due to depletion of [diol] (Eqn. 2). The decreased rate may also be explained on the basis of a reaction between the species of the type $Ce(OH)(NO_3)_3$ [instead of simple $Ce(NO_3)_4$] and diol. But it was shown by Blaustein and Gryder²⁷ that in HNO_3 solutions of Ce^{4+} hydrolytic equilibrium was absent and therefore formation of $Ce(OH)(NO_3)_3$ type of species under our experimental conditions is not likely. The type of mechanism suggested for the oxidation of alcohols, through the formation of Ce^{4+} -alcohol complex which unimolecularly dissociated in a rate determining step is to be ruled out for HCHO oxidation under our experimental conditions since, $1/k_{\text{pseudo}}$ vs. $1/[HCHO]$ plots were linear passing through the origin (Fig. 1c). At higher concentrations of Ce^{4+} and HCHO where a slight intensification of the colour (probably due to complex formation) was no doubt noticed but the rate was too fast to be followed under those conditions. Absence of complex formation at low concentrations used, was also proved by an independent optical method; the observed optical densities of solution of Ce^{4+} -HCHO were equal to those of Ce^{4+} - H_2O . Ce^{4+} in equations (3) and (4) represents $Ce(NO_3)_4$ the active species involved in the reaction and not $Ce^{4+}_{(aq.)}$. The rate determining step (3) has been assumed to involve the O-H bond fission. It should be pointed out, however, that the α -C-H bond fission is equally likely. The controversy regarding α -C-H or O-H bond fission is not yet resolved,^{21-23, 30} unambiguously. Recently Trahanovsky and Young³⁴ suggested the possibility of two-electron transfer in Ce^{4+} oxidations of toluenes leading to Ce^{2+} and an ionic intermediate $Ar\cdot\overset{+}{C}H_2$ and the former reacted with Ce^{4+} to give $2Ce^{3+}$. In view of the fact that polymerization of vinyl monomers by ceric salts³⁵ proceed by free radicals, the mechanism of Trahanovsky *et al.* involving ionic intermediates appeared to be not likely.

(vi) *The rate law.*—The rate law (5) may be significant:

$$-R_{Ce^{4+}} = k_{\text{obs.}} [Ce^{4+}]_t [HCHO]_t = k_2 [Ce^+]_e [Diol]_e \quad (5)$$

the subscripts t 's and e 's refer to total and equilibrium concentrations respectively. In HNO_3 medium the reactive species of Ce^{4+} during oxidation of secondary alcohols¹⁹ was established to be neutral ceric nitrate molecule $Ce(NO_3)_4$, which with added NO_3^- may form $Ce(NO_3)_5^-$ and $Ce(NO_3)_6^{2-}$ species:





Assuming that

$$[\text{Ce}^{4+}]_e \approx [\text{Ce}(\text{NO}_3)_4] \quad \text{and} \quad [\text{Ce}(\text{NO}_3)_6]^{2-} \approx [\text{Ce}^{4+}]_t.$$

It is shown that

$$[\text{Ce}^{4+}]_e = \frac{[\text{Ce}^{4+}]_t}{K_5 K_6 [\text{NO}_3^-]^2} \quad (5 a)$$

and

$$[\text{doli}]_e = \frac{[\text{HCHO}]_t}{1 + K_2 [\text{H}^+]} \quad (5 b)$$

Substitution of 5 (a) and 5 (b) into (5) we get

$$k_{\text{obs.}} = \frac{k_2}{K_5 K_6 [\text{NO}_3^-]^2 (1 + K_2 [\text{H}^+])}$$

or

$$\frac{1}{k_{\text{obs.}}} = \left(\frac{K_5 K_6 [\text{NO}_3^-]^2}{k_2} \right) + \frac{K_2 [\text{H}^+]}{k_2} \quad (8)$$

which explains the observed proportionalities of $k_{\text{obs.}}$ to $[\text{NO}_3^-]$ and $[\text{H}^+]$.

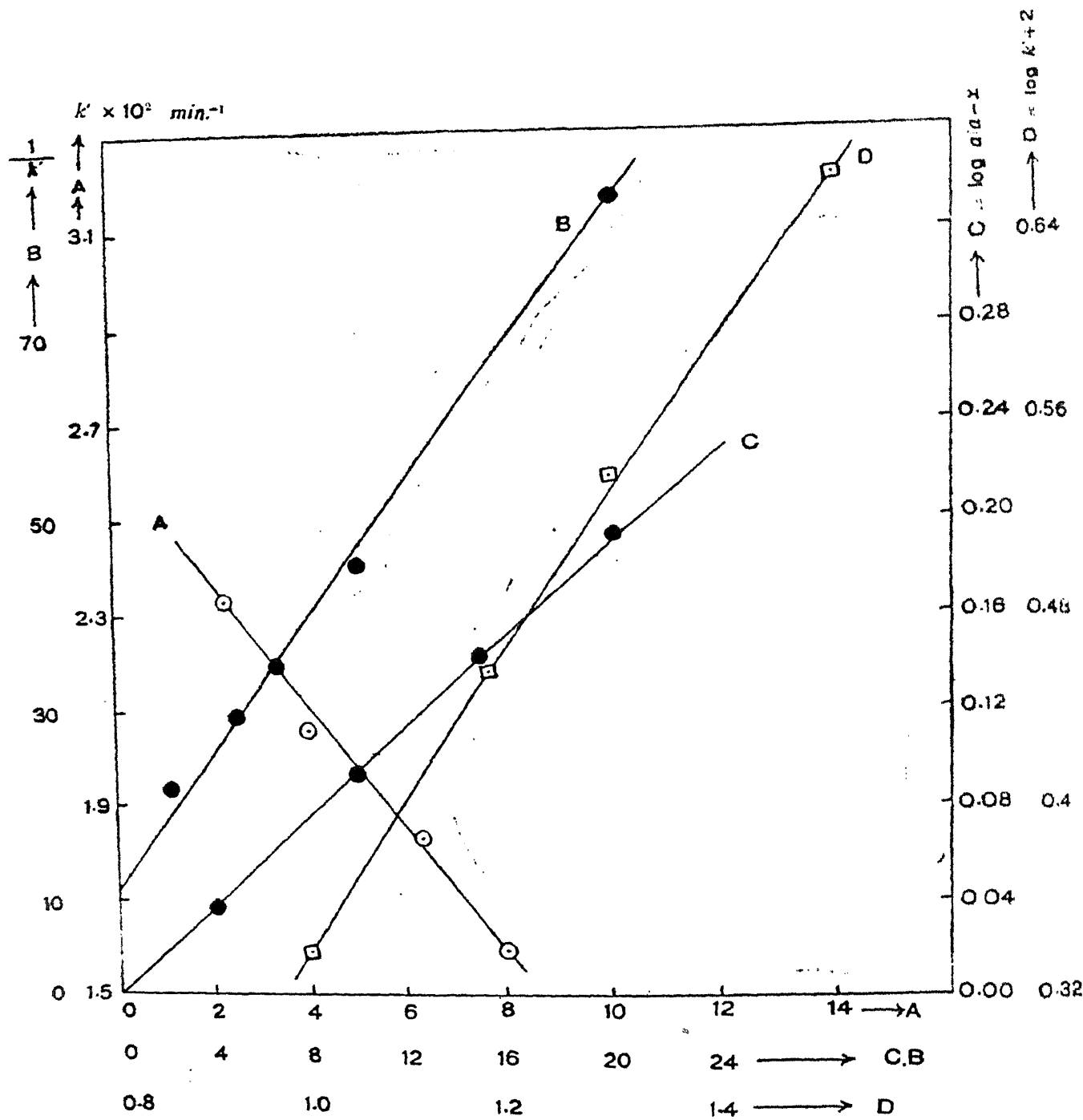
(vii) *Evaluation of rate constants.*—(a) From plots of $1/k_{\text{obs.}}$ vs. $[\text{H}^+]$ at constant $[\text{NO}_3^-]$, slope/intercept = $K_2 = 0.92 (\text{m./l})^{-1}$ at 20°C. was obtained [cf. $K_2 = 0.7 (\text{m./l})^{-1}$ at 22°C. by Hargreaves and Sutcliffe⁴].

(b) From plots of $\log k_{\text{obs.}}$ vs. $1/T$ the overall activation energy 21.9 K. Cals. was obtained. The reported ΔE values for the oxidation of HCHO by Ce^{4+} in sulphuric and perchloric acid media are 29 ± 2 K. Cal. and 16 ± 3 K.cals. respectively.⁴ The order of ΔE is similar to the order of oxidation potentials of $\text{Ce}^{3+}/\text{Ce}^{4+}$ couple in the three acid media.

2. Oxidation of Alcohols

The oxidation of alcohols, *n*-propanol, allyl alcohol, cyclo-hexanol follow the usual pattern,^{11, 12} of Ce^{4+} -alcohol complex formation which dissociated subsequently. A different behaviour, however, was observed

* Recent studies on the co-ordination number of Ce^{4+} indicate it to be eight,³⁰ though ceric ammonium nitrate was found to exist as a hexanitratecerate anion $\text{Ce}(\text{NO}_3)_6^{2-}$ by Meyer and Jacoby.³¹ This has received proof from X-ray studies also.³² Hence we prefer equilibria (6) and (7) only.

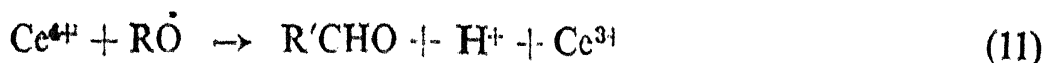
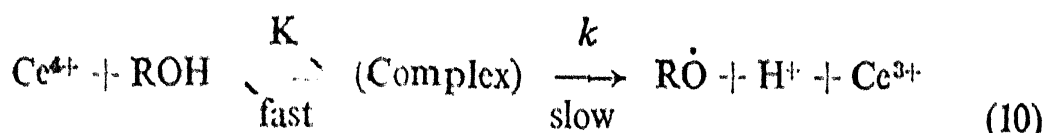


$$A = [\text{NO}_3^-]^2 \text{ (m/e)}^2; B = \frac{1}{[\text{ROH}]}; C = \text{Time in minutes};$$

$$D = \log [\text{ROH}] + 2$$

FIG. 2. (a) Effect of $[\text{NO}_3^-]$ on the rate constant k' . Plot of $k' \times 10^2 \text{ min.}^{-1}$ vs. $[\text{NO}_3^-]^2$. $[\text{Ce}^{4+}] = 6 \times 10^{-3} \text{ M}$; $[\text{H}^+] = 1.0 \text{ M}$; $[n\text{-propanol}] = 0.15 \text{ M}$; Temperature = 22° C . (b) Evidence for complex formation. Plot of $1/k'$ vs. $1/[n\text{-propanol}]$. $[\text{Ce}^{4+}] = 6 \times 10^{-3} \text{ M}$; $[\text{HNO}_3] = 1.0 \text{ M}$; Temperature = 22° C . (c) Order of $[\text{Ce}^{4+}]$ in $-d\text{Ce}^{4+}/dt$ with $n\text{-propanol}$ as substrate. Plot of $\log a/(a-x)$ vs. time in minutes. $[\text{Ce}^{4+}] = 6 \times 10^{-3} \text{ M}$; $[\text{HNO}_3] = 1.0 \text{ M}$; $[n\text{-propanol}] = 0.1 \text{ M}$; Temperature = 22° C . (d) Order of $[n\text{-propanol}]$ in $-d\text{Ce}^{4+}/dt$. Plot of $\log k' + 2$ vs. $\log [\text{ROH}] + 2$; $[\text{Ce}^{4+}] = 6 \times 10^{-3} \text{ M}$; $[\text{HNO}_3] = 1.0 \text{ M}$; Temperature = 22° C .

with benzyl alcohol. In ceric ion oxidations of *n*-propanol, allyl alcohol and cyclohexanol the order of [alcohol] was less than one; $1/k_{\text{pseudo}}$ vs. $1/[\text{alcohol}]$ were straight lines with intercepts (Fig. 2, *a-d*) on the ordinates indicating that the mechanism of oxidation conformed to Michaelis and Menton type (*cf.* secondary alcohols¹²). We therefore invoke the mechanism



Various alternative possibilities suggested for step (3) for HCHO are also applicable for the slow step (10).

If

$$-R_{\text{Ce}^{4+}} = k [\text{Ce}^{4+}]_e [\text{ROH}]_e = k_{\text{pseudo}} [\text{Ce}^{4+}]_t$$

it may be shown that

$$k_{\text{pseudo}} = \frac{kK [\text{ROH}]}{(1 + K [\text{ROH}]) K_5 K_6 [\text{NO}_3^-]^2}$$

or

$$1/k_{\text{pseudo}} = \frac{K_5 K_6 [\text{NO}_3^-]^2}{kK [\text{ROH}]} + \frac{K_5 K_6 [\text{NO}_3^-]^2}{k} \quad (12)$$

The observed proportionalities between $1/k_{\text{obs}}$ vs. $[\text{NO}_3^-]^2$ (Fig. 2 *a*) and $1/[\text{ROH}]$ (Fig. 2 *b*) therefore are understandable. k_{pseudo} is the pseudo-unimolecular rate constant and $[\text{ROH}]$ total alcohol concentration, K the formation constant of the Ce^{4+} -alcohol complex and k the rate constant. The effect of increased H^+ , however, was found to inhibit the overall rate of oxidation of *n*-propanol by 40% ($k = 3.4 \times 10^{-2} \text{ min.}^{-1}$ at $[\text{H}^+] = 0.5 \text{ M}$; $k_{\text{pseudo}} = 1.95 \times 10^{-2} \text{ min.}^{-1}$ $[\text{H}^+] = 2.5 \text{ M}$) at constant ionic strength $\mu = 2.8 \text{ M}$ but H^+ had no effect on cyclohexanol oxidation. In perchloric acid medium it was observed, however that the rate increased with increase in $[\text{H}^+]$ for secondary¹⁹ as well as primary alcohols¹⁰ and also for aldehydes.⁴ This was explained on the basis that in perchloric acid medium $\text{Ce}_{(\text{aq.})}^{4+}$ was the active species and that with increased $[\text{H}^+]$, the hydrolysis equilibrium was shifted towards $\text{Ce}_{(\text{aq.})}^{4+}$ side. But in HNO_3 medium the hydrolysis equilibrium is absent.²⁸ The decrease of rate with increased of $[\text{H}^+]$ for primary alcohols in HNO_3 medium is, however, not clear. The formation constant K was found to be the same at different

$[\text{NO}_3^-]$ indicating that NO_3^- is not displaced during complex formation. In the case of benzyl alcohol oxidation no complexing was observed with Ce^{4+} . The order of [Benzyl alcohol] was found to be strictly one and the

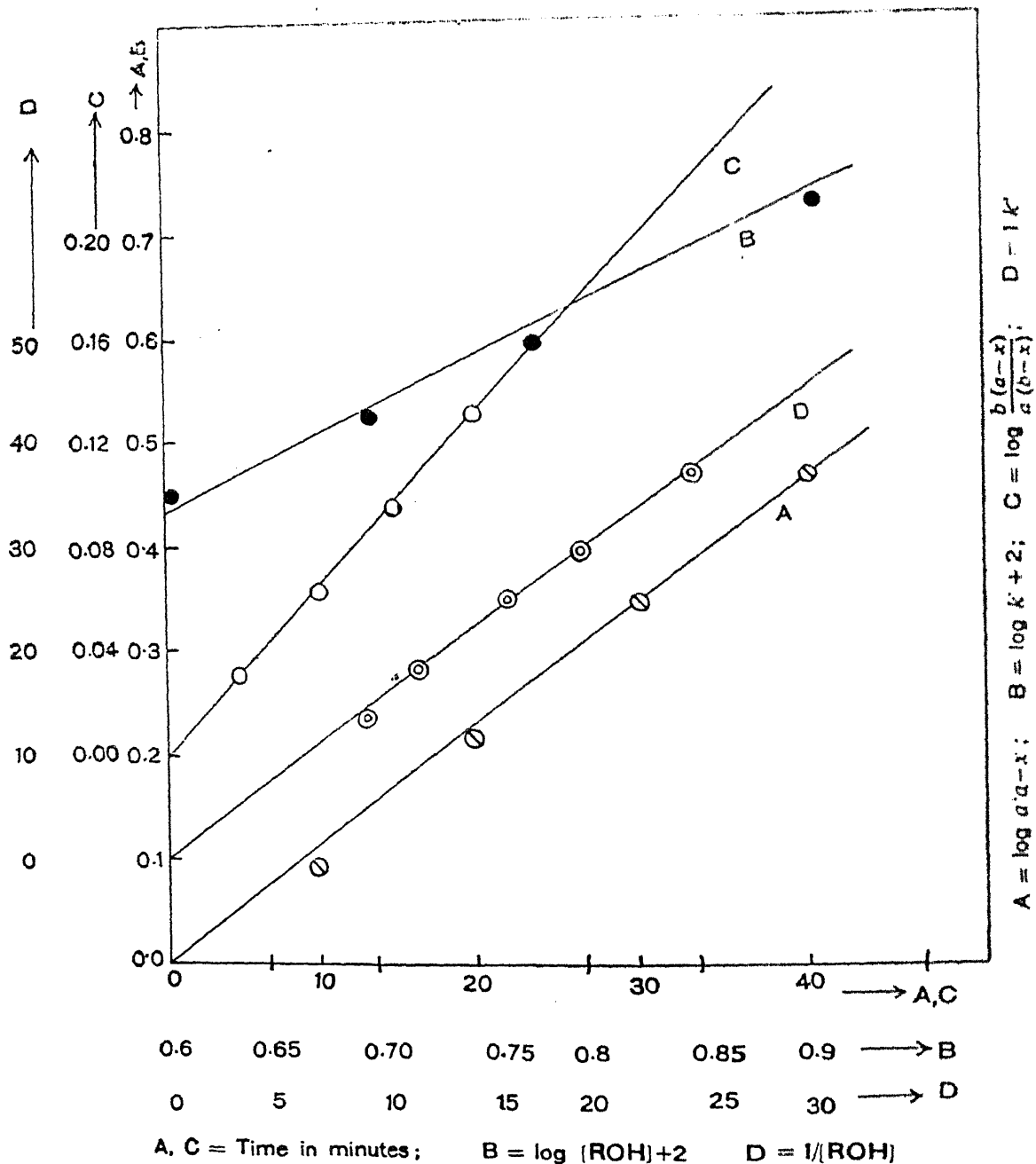


FIG. 3. (a) Order of $[\text{Ce}^{4+}]$ in $-d\text{Ce}^{4+}/dt$ with benzyl alcohol as substrate. Plot of $\log a/(a-x)$ vs. time in minutes. $[\text{Ce}^{4+}] = 3 \times 10^{-3} \text{M}$; [Benzyl alcohol] = 0.04M ; $[\text{HNO}_3] = 1.0 \text{M}$; Temperature = 22°C . (b) Order of [Benzyl alcohol]. Plot of $\log k' + 2$ vs. $\log [\text{ROH}] + 2$. $[\text{Ce}^{4+}] = 4 \times 10^{-3} \text{M}$; Temperature = 22°C ; $[\text{HNO}_3] = 1.0 \text{M}$. (c) Verification of the overall order. Plot of $\log b(a-x)/a(b-x)$ vs. time in minutes. $[\text{Ce}^{4+}] = 0.02 \text{M}$; [Benzyl alcohol] = 0.04M ; Temperature = 30°C . $[\text{HNO}_3] = 1.0 \text{M}$. (d) Search for the complex. Plot of $1/k'$ vs. $1/[\text{ROH}]$. Conditions same as for (b).

plot $1/k_{\text{pseudo}}$ vs. $1/[\text{ROH}]$ was linear with no intercept (Fig. 3, *b, d*). Further the absorption spectra of ceric nitrate and ceric nitrate-benzyl alcohol mixture were found to be the same under our experimental conditions. The overall order was found to be two (Fig. 3 *c*). Activation parameters for the alcohol studies are given in Table I.

TABLE I

| Substrate | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|--------------------|-----------|------|------|-------|----|------|------|-----|-----|
| Allyl alcohol | ... 11.00 | 26.2 | 25.1 | 19.19 | 23 | 2.78 | 10.4 | -31 | -60 |
| <i>n</i> -propanol | .. 2.88 | 25.4 | 24.2 | 20.70 | 11 | 2.31 | 6.7 | -21 | -50 |
| Cyclohexanol | ... 3.90 | 23.8 | 22.6 | 20.5 | 6 | 0.32 | 9.8 | -33 | -21 |
| Benzyl alcohol | .. 1.05 | 24.2 | 23.0 | 21.3 | 5 | — | ... | — | ... |

1. k^* (lit./mol.) sec^{-1} at $22^\circ \text{C} \times 10^3$
2. ΔF^\ddagger K. Cals./mol.
3. ΔH^\ddagger K. Cals./mol.
4. ΔF^\ddagger K. Cals./mol.
5. ΔS^\ddagger e.u.

6. K lit./mol.
7. $-\Delta H^\ddagger$ K. Cals./mol.
8. ΔS^\ddagger e.u.
9. ΔF^\ddagger Cals./mol.

* ΔH^\ddagger was calculated using the equation $\Delta H^\ddagger = \Delta F^\ddagger + nRT$.
 k^* Initial rate/[Ce^{4+}] [substrate] for all alcohols.

The constancy in ΔF^\ddagger for all the alcohols studies may be explained on the basis of isokinetic relationship,³³ that for a series of compounds of slightly different structure but undergoing a reaction essentially be the same mechanism, the ΔF^\ddagger may be more or less constant with relative changes in ΔE^\ddagger and ΔS^\ddagger .

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