Kinetic Study of the Oxidation of *tert*-Butanol by Cerium(IV) in Perchloric Acid Media

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Abstract. The kinetics of the oxidation of *tert*-butanol by cerium(IV) in perchloric acid has been investigated spectrophotometrically. The water role has been elucidates by using acidity criteria. A tentative mechanism consistent with the kinetics is discussed where a complex cerium(IV)-alcohol is formed, the equilib

rium constant for its formation being calculated. The ratedetermining step is a bimolecular process between ions of positive charge.

Keywords: Cerium; Oxidations; Kinetics

Kinetische Untersuchung der Oxidation von *tert*-Butanol durch Cer(IV) in Perchlorsäure

Inhaltsübersicht. Die Kinetik der Oxidation von *tert*-Butanol durch Cer(IV) in Perchlorsäure-Lösung wurde spektrophotometrisch untersucht. Die Rolle des Wassers wurde durch Anwendung von Säure-Kriterien aufgeklärt. Es wird ein Mechanismus diskutiert,

bei dem ein Cer(IV)-Alkohol-Komplex gebildet wird und dessen Gleichgewichtskonstante wird berechnet. Der geschwindigkeitsbestimmende Schritt ist ein bimolekularer Prozeß zwischen Ionen positiver Ladung.

Introduction

The use of cerium(IV) compounds as a quantitative colorimetric reagent in the analysis of alcohols it is well known [1, 2]. The colorimetric technique is based on the formation of Ce^{IV}-alcohol complexes. It has been demostrated that these complexes are 1:1 complexes that involve one molecule of alcohol and one Ce^{IV} species. It is also well-establised that the complex formation attains the equilibrium state very quickly [3–5] and a number of formation constants for Ce^{IV} complexes for simple alcohols and glycols have been reported [6–8].

Concerning the reaction mechanism, *Ardon* [9] detected that acetaldehyde is formed in the Ce^{IV} oxidation of ethanol; the process being preceded by the formation of a reversible complex followed by its monomolecular decomposition. The complex formation was not evidenced in the Ce^{IV} oxidation of pinacol [10] but its existence was shown for ceric oxidation of glycerol [11]. However, that result for pinacol appears to be more a consequence of the experimental conditions than a structure effect. In fact, the fission of the C–C bond is the process operating in the mechanism of the pinacol oxidation [12] instead of the oxidation of :CHOH to :C=O in alcohols. The first mechanism appeared to require the formation of chelate complexes. On the other hand, *Young* and *Trahanovsky* [13] con-

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clude from the determination of the formation constants for a number of cerium(IV)-alcohol complexes that the constant values are independent of the molecular environement of the hydroxyl group of the alcohol molecule. All these arguments permit to conclude that complexes formation is a general feature of the Ce^{IV} oxidation of alcohols.

Efforts have been made elucidating the oxidation mechanisms for both primary and secundary alcohols but little attention has been paid to the oxidation of tertiary alcohols. One exception is the work of *Littler* and *Waters* [14] who found that the rates of oxidation of *tert*-butanol, are very small as compared with other alcohols.

On the other hand, a plot of the formation constants for cerium(IV)-alcohol complexes against the formation constants for Cr^{VI} -alcohol complexes shows a good correlation [13] but the point for *t*-BuOH has to be excluded. This fact is very difficult to justify although this alcohol is much more sterically hindered than the others.

Hence, the oxidation of *t*-BuOH appears to be singular. For this reason, the aim of the present work has been to widen this field carrying out a conventional study of the kinetics of the Ce^{IV} oxidation of *t*-BuOH in an unproblematic solvent as perchloric acid.

Results and Discussion

Analysis of the Findings

The location of the absorption band corresponding to the chemical of control, Ce^{IV}, depends on the nature of the solvent. In perchloric acid the band is located at 290 nm, but

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Table 1 Influence of the concentration of the oxidant species, Ce^{IV} , on the rate constant, k_r .

c(t-BuOH) = 0.1 mol dm	DH = 0.1 mol dm ⁻³ , c(HClO ₄) = 2.0 mol dm ⁻³ and T = 30 °C				
$10^4 \text{ c(Ce^{IV})/mol dm}^{-3}$	$10^4 \text{ k}_{\text{r}}(\pm 0.02)/\text{s}^{-1}$	r _{xy}			
3.0	3.68	0.9999			
4.0	3.70	0.9999			
5.0	3.66	0.9998			
6.0	3.70	0.9997			
7.0	3.74	0.9998			
8.0	3.68	0.9996			



Figure 1 Variation of the rate constant, k_r with the *t*-BuOH concentration. [Ce^{IV}] = 6 x 10⁻⁴ M and T = 30 °C; 1) [HClO₄] = 1.0 M; 2) [HClO₄] = 2.0 M and) [HClO₄] = 3.0 M.

Table 2 Influence of the ionic strength on the rate constant, k_r .

	r _{xy}
c(NaClO ₄ /mol dm ⁻³ I/mol dm ⁻³ $10^4 k_r(\pm 0.02)/s^{-1}$	
0.0 2.0 3.27	0.9997
0.5 2.5 4.23	0.9999
1.0 3.0 5.02	0.9999
1.5 3.5 5.94	0.9997
2.0 4.0 7.28	0.9999
2.5 4.5 7.84	0.9998

if sulfate ions are present in the solvent, it is located at 320 nm. These results point to the formation of different complexes between the Ce^{IV} species and the anion of the acid as was also found by other workers [15, 16].

It was observed that in order for the $Ce^{IV} \rightarrow Ce^{III}$ evolution to take place at a mensurable rate, it is necessary for

the *t*-BuOH concentration to be in excess with regard to the concentration of the oxidant species, this being the only concentration which changed appreciably during the course of the reaction. The values of the experimental rate constant, k_p were obtained by the integration method using the first order equation, the linear correlation coefficients, r_{xy} , of the adjustment being better than 0.999 in all cases.

A series of experiments was carried out in which the concentrations of all the reagents remained constant except the Ce^{IV} concentration which was modified systematically. The results obtained are shown in Table 1 where it can be observed that the k_r values remain practically constant. This actually means a true first-order dependence of the reaction rate on the Ce^{IV} concentration.

In order to study the influence of the t-BuOH concentration on the reaction rate, a series of experiments was performed in which the initial concentration of the reducer was varied in the range from 0.02 to 0.20 mol dm^{-3} , and the initial concentrations of the rest of the reagents remained constant. This was done for three different concentrations of perchloric acid. The results obtained for the rate constant, k_p show that as the *t*-BuOH concentration increases, so does the rate of the reaction. When analyzing the dependence of these k_r values on the concentration of the reducer, linear correlations where obtained when plotting $1/k_r$ vs. $1/k_r$ c(t-BuOH)_T as can be observed in Fig. 1. This seems to indicate the formation of a complex between the oxidant species, Ce^{IV} , and the reducer species, *t*-BuOH, followed by its subsequent decomposition in a kinetic step. It is consistent with the generally accepted mechanism for CrVI oxidation of alcohols [17], so that ceric oxidations are reminiscent of chromic acid oxidations.

In order to understand the influence of the ionic strength, I, on the reaction rate (I-effect), a series of experiments was carried out in which the concentrations of the oxidant (6 x $10^{-4} \text{ mol dm}^{-3}$) and reducer (0.10 mol dm⁻³) species, the perchloric acid concentration (2.0 mol dm⁻³) and temperature (30 °C) remained constant, the concentration of so-dium perchlorate being varied systematically up to 2.5 mol dm⁻³ (as the perchlorate ions do not form complexes with Ce^{IV} species). Table 2 shows the results obtained. A gradual increase in the rate was observed when adding sodium perchlorate. When analysing the results that were found, the rate constant values fit the following equation (r_{xy} = 0.9975):

$$\log k_{\rm r} = -5.89(\pm 0.10) + 4.12(\pm 0.16)\sqrt{I/(1+\sqrt{I})}$$
(1)

where the origin ordinate actually is the logarithm of the corrected rate constant for the I-effect, $k_r(0)$. This result strongly suggests the existence of a kinetic salt effect for the reaction. The unambigous positive value of the $z_+ \times z_-$ product shows also that the ions that participate in the rate-determining step are the same sign.

A series of experiments was performed in which the ionic strength of the solvent, I, was modified with another electrolyte, namely different amounts of sodium sulfate (the concentration of the oxidant species in this case was fol-



Figure 2 Influence of the concentration of sulfate ions on the rate constant, k_r . [Ce^{IV}] = 6 x 10⁻⁴ M, [*t*-BuOH] = 0.14 M, [HClO₄] = 2.0 M and T = 30 °C.

Table 3 Influence of the solvent acidity on the rate constant, k_r .

$(\text{Ce}^{IV}) = 6 \times 10^{-4} \text{ mol dm}^{-3}, \text{ c}(;-\text{t}-\text{BuOH}) = 0.1 \text{ mol dm}^{-3}, \text{ I} = 2.5 \text{ mol dm}^{-3}, \text{ and } \text{T} = 20.9 \text{ c}$					
$c(HClO_4)/mol dm^{-3}$	c(NaClO ₄)/mol dm ⁻³	$10^4 \text{ k}_{\text{r}}(\pm 0.02)/\text{s}^{-1}$			
1.0	2.5	5.50			
1.5	2.0	5.83			
2.0	1.5	5.94			
2.5	1.0	6.38			
3.0	0.5	6.59			
3.5	0.0	6.78			

lowed at 320 nm instead of 290 nm due to the formation of complexes between Ce^{IV} species and sulfate ions). The results are shown in Fig. 2, where it can be seen that as the concentration of sodium sulfate increases, the rate constant decrease until it remains practically constant.

The effect of the acidity of the solvent on the reaction rate was also investigated. The temperature and concentrations of the oxidant and reducer species were fixed, varying the concentration of perchloric acid in the range from 1.0 to 3.5 mol dm⁻³ while keeping the ionic strength constant at I = 3.5 mol dm⁻³. The results for the experimental rate constant are shown in Table 3, the k_r values being corrected for the I-effect (k_r(0) values). It can be observed that as the concentration of perchloric acid increases so does the k_r(0) which means that the reaction behaves like a acid catalysed reaction.

In order to clarify the nature of the rate-determining step of the reaction mechanism, the Zucker-Hammer hypothesis



Figure 3 Application of the Zucker-Hammett criteria. $[Ce^{IV}] = 6 \times 10^{-4} \text{ M}, [t-BuOH] = 0.1 \text{ M}, I = 3.5 \text{ M NaClO}_4/$ HClO₄ and T = 30 °C.

Table 4 Influence of the concentration of Ag^+ on the rate constant, $k_{\rm r}.$

$c(Ce^{IV}) = 6 \times 10^{-4} \text{ mol dm}^{-3}$, $c(HClO_4) = 1.0 \text{ mol dm}^{-3}$, $c(^{1}BuOH) = 0.12 \text{ mol dm}^{-3}$ and $T = 30 ^{\circ}C$				
$10^4 \text{ c(Ag^+)/mol dm}^{-3}$	$10^4 k_r(\pm 0.02)/s^{-1}$	r _{xy}		
0.0	2.86	0.9998		
2.0	2.78	0.9990		
4.0	2.56	0.9984		
6.0	2.48	0.9975		
8.0	2.32	0.9988		
10.0	2.12	0.9981		

Table 5 Analysis of the $1/k_r$ vs. 1/c(t-BuOH) plotts.

$c(Ce^{IV}) = 6 \times 10^{-4} \text{ mol dm}^{-3} \text{ and } T = 30 ^{\circ}C$				
c(HClO ₄)/	$10^4 k_8 c(H^+)/dm^{-3}$	K_7	r _{xy}	
mol dm ⁻³	$mol^{-1} s^{-1}$			
1.0	4.71	11	0.9998	
2.0	6.77	10	0.9994	
3.5	13.29	11	0.9996	

[18] was initially considered. When plotting log $k_r(0)$ vs. H_0 (the Hammet acidity function) a straight line was obtained (Fig. 3), the gradient of which -0.034 ± 0.006 ($r_{xy} = 0.9922$) is noticeably different from one. Therefore, the Bunnet-Olsen criteria [19] were then applied. When plotting (log $k_r(0) + H_0$) vs. ($H_0 + \log c(H^+)$) a good straight line ($r_{xy} = 0.9989$) was found as Fig. 4 shows, the gradient of which is



Figure 4 Application of the Bunnett-Olsen criteria at the same conditions of Figure 3

 $\Phi = 1.25 \pm 0.12$. From these results it may be deduced that the rate-determining step is bimolecular and the gradient value suggests to that water acts as a proton transfer agent.

Finally, the rate of the reaction between *t*-BuOH and Ce^{IV} in the presence of Ag^{I} ions has been monitored. The experimental results are shown in Table 4. It can be seen that the rate constant value decreases when silver ions are added.

Formal Mechanism

Several studies [20, 21] have found that Ce^{IV} species present in perchloric acid as solvent are Ce^{4+} , $Ce(OH)^{3+}$ and $Ce(OH)_2^{2+}$. In addition, the hydrolysis constants at ionic strength I = 1 mol dm⁻³ have been determined using spectrophotometric techniques [22]:

$$Ce^{4+} + H_2O \iff Ce(OH)^{3+} + H^+$$
 $K_3 = 6.40$ (2)

$$\operatorname{Ce}(\mathrm{OH})^{3+} + \operatorname{H}_2\mathrm{O} \iff \operatorname{Ce}(\mathrm{OH})_2^{2+} + \operatorname{H}^+ \qquad \mathrm{K}_4 = 0.12 \qquad (3)$$

However, in this work, given the value of the solvent acidity for the experiments, the dominant form for the oxidant is $Ce(OH)^{3+}$. On the other hand, if sulfate ions are added to the solvent, new species of Ce^{IV} are formed which are the mono, di and tri sulfato complexes whose formation equilibria [22] are the following:

$$\operatorname{Ce}^{4+} + \operatorname{SO}_4^{2-} \longleftrightarrow \operatorname{Ce}(\operatorname{SO}_4)^{2+} \qquad \qquad \operatorname{K}_5 = 3500$$
 (4)

$$\operatorname{Ce}(\operatorname{SO}_4)^{2+} + \operatorname{SO}_4^{2-} \rightleftharpoons \operatorname{Ce}(\operatorname{SO}_4)_2 \qquad \operatorname{K}_6 = 200 \tag{5}$$

$$\operatorname{Ce}(\operatorname{SO}_4)_2 + \operatorname{SO}_4^{2-} \longleftrightarrow \operatorname{Ce}(\operatorname{SO}_4)_3^{2-} \qquad \operatorname{K}_7 = 50 \tag{6}$$

Concerning the reducer species, *t*-BuOH, it is well known that for tertiary alcohols the oxidation begins on the carbon atom linked to the hydroxyl group. On the other hand, the stoichiometric equation shows that both acetone and formaldehyde are produced.

Bearing all these facts in mind as well as the experimental results obtained in perchloric acid, the following reaction mechanism can be proposed:

$$Me_3COH + Ce^{4+} \iff Comp$$
 (7)

$$\operatorname{Comp} + \operatorname{H^{+}} \xrightarrow{fast} [\operatorname{Me_3COH_2} \cdot]^{2+} + \operatorname{Ce^{3+}} X$$
(8)

$$\begin{bmatrix} Me_3COH_2 \cdot]^{2+} + H_2O \iff [Me_3COH_2 \cdot H_2O]^{2+} \\ X X H_2O \end{bmatrix}$$
(9)

$$Ce^{4+} + [Me_3COH_2 \cdot H_2O]^{2+} \xrightarrow{slow} Me_2CO + MeOH + Ce^{3+} + 3H^+ X \cdot H_2O$$
(10)

$$MeOH + 2Ce^{4+} \longrightarrow HCHO + 2Ce^{3+} + 2H^{+}$$
(11)

If one takes into consideration the fact that all the experiments were performed in the presence of an excess of t-BuOH, it is reasonable to think of the formation of complexes Comp, where Ce^{IV} participates together with t-BuOH species. $Ce(OH)^{3+}$ is likely to be the major active species although the other Ce^{IV} species may also be active. Sulfate ions, like nitrate ions [13], are competing with alcohol molecules for Ce^{IV} coordination sites in order to give the complex Comp; that explaining the results of Fig. 2. The formation of the complex Comp is similar to that proposed by other researches [23] in the ceric oxidation of both primary and secundary alcohols. Besides, in our cases, there is experimental evidence of the existence of the complex Comp. It should be remembered that the inverse of the experimental rate constant versus the inverse of the 'BuOH concentration is linear (Fig. 1).

Actually, the process of eq. (7) is a pre-equilibrium interaction to produce the intermediate precursor, Comp. The oxidation of *t*-BuOH may therefore be considered to occur through one electron transfer from *t*-BuOH to Ce^{IV} inside the Comp structure in a fast step which is acid catalyzed (eq. (8)). The cationic radical species X is the first intermediate and X·H₂O is its hydrated form (second intermediate). It is probable that the bond between the alcohol and Ce^{IV} is mainly electrostatic. In fact, stable complexes of rare earth metal ion show electrostatic bonding rather than stronger covalent bonding [24].

The process of eq. (10) has been considered to be the rate -determining step. It consists of the Ce^{4+} attack on the electron-deficient oxygen atom in the X·H₂O structure with the release of protons. Two important features support this asumption. First, from the application of the Bunnett-Olsen

criteria it was shown that water acts as a proton transfer agent. Moreover, the existence of an unambigous salt effect was proved, the z_+z_- product being positive.

It has been assumed that the step of eq. (7) attains the equilibrium state very quickly [3-5], the equilibrium constant being K₇. Hence, the concentration of complexes Comp is:

$$[\text{Comp}] = \frac{K_7[\text{Me}_3\text{COH}]_T[\text{Ce}^{4+}]}{1 + K_7[\text{ME}_3\text{COH}]_T}$$
(12)

On the other hand, it has been considered that both intermediates are in the steady-state conditions (as it seems rasonable because they are radical species). Therefore the following equations can be derived:

$$\frac{d[X]}{dt} = k_8[\text{Comp}][\text{H}^+] - k_9[X][\text{H}_2\text{O}] + k_{-9}[X \cdot \text{H}_2\text{O}] = 0$$
(13)

$$\frac{d[X \cdot H_2 O]}{dt} = k_9[X][H_2 O] - k_{-9}[X \cdot H_2 O] - k_{-10}[X \cdot H_2 O][Ce^{4+}] = 0 \quad (14)$$

Thus, from eqs. (12), (13) and (14) together with that the rate-determining step, process of eq. (10) the following rate equation can be derived:

$$v_{r} = k_{10} [Ce^{4+}] [X \cdot H_{2}O] = \dots = k_{8} \frac{K_{7} [BuOH]_{T}}{1 + K_{7} [BuOH]_{T}} [H^{+}] [Ce^{4+}]$$
(15)

where k_8 is the rate constant for the step of eq. (8); but for the reasons given before the process of eq. (8) is not the limiting step.

Equation (15) accounts for the kinetic order with respect to Ce^{IV} species and also for the dependence of k_r on the ^tBuOH concentration (Fig. 1). From the origin ordinate and the gradient of these plotts, the values of the rate constant $k_8[H^+]$ and the equilibrium constant K_7 can be, obtained, respectively, the results of which are shown in Table 5. These findings demostrate that the equilibrium constant for the formation of the complex Comp is independent from the solvent acidity whereas the rate constant for the complex descomposition clearly depends on acidity; this is an additional support for the mechanism formulation. It should be noted, however, that these values are apparent equilibrium constant since they measure the position of the equilibrium of all ceric species with alcohol to form a 1:1 Ce^{IV}-alcohol complex. Some authors [3] have attempted to derive a true equilibrium constant which is acid and ligand independent since the nature of the ceric species in solution is a function of the experimental conditions (mainly the solvent acidity but also the added ligands).

On the other hand, the low value that was found for the z_+z_- product (as compared with that was expected) can be explained because k_8 is actually the rate constant conditioning the phenomenological characteristics for the salt kinetic effect; the step of eq. (8) being a process between two ions of charge +4 and +1 respectively.

Finally, the inhibition effect that AgI species produces on the reaction could be explained through the formation of an adduct, A, between the intermediate X and Ag^+ ions:

$$\underset{X}{\text{Me}_{3}\text{COH}_{2}} \cdot \overset{2^{+}}{\longrightarrow} + \text{Ag}^{+} \overleftrightarrow{\longrightarrow} \text{A}(\text{Ag}^{2^{+}}) + \text{H}^{+}$$
(16)

The formation of similar compounds has been reported for the Ag^I catalyzed oxidation of dimethylsulfoxide, DMSO, by ceric species [25]. Given that DMSO has a similar structure like ^tBuOH this appears to be reasonable asumption. The adduct formation produces the change of the steadystate conditions for X, its concentration being now controlled by the equilibrium of eq. (16). Hence, the rate constant decreases when Ag^I species are added to the reaction mixture as Table 4 shows.

Experimental Part

The reagents used were tert-butanol, *t*-BuOH, ammonium and cerium(IV) nitrate, sodium perchlorate, silver nitrate and sodium sulfate from Merck p. a., and perchloric acid (60 %, $d = 1.18 \text{ g cm}^{-3}$) from Panreac p. a. Brady's reagent (70 %) and CDCl₃ were from Aldrich. All the experiments were performed in aqueous media (water twice distilled). The Ce^{IV} stock solutions were standardised with ammonium Fe^{II} sulfate solution using ferroin as indicator. Under the experimental conditions employed, Ce^{IV} solutions are kinetically and thermodynamically highly stable. *Tert*-butanol was used after redistillation under reduced pressure. The stock solutions were tested using a potassium iodine solution acidified with hydrochloric acid [26].

The reactions were carried out under the following experimental conditions: $c(^{t}BuOH)_{T} \ge c(Ce^{IV})_{T}$, where $c(^{t}BuOH)_{T}$ and $c(Ce^{IV})_{T}$ give the total 'BuOH and Ce^{IV} concentrations, respectively.

Kinetic runs were followed spectrophotometrically using a Spectronic 1201 (200-800 nm). The progress of the reaction was followed at 290 nm (for perchloric acid as solvent) or alternatively at 320 nm when sulfate ions was added. The reactor was a special quarz cell (with 1 cm of optic pathway), supplied with an internal system of thermostation connected to a Heto cryostat which ensures temperature stability during the reaccion runs with an error of ± 0.05 °C. The rate constant (k_r) values were reproducible within the experimental error limit. No effect on k_r was observed by the addition of the reaction products. Average values of at least three independent determinations of k_r were taken.

Under the kinetic conditions, i.e. $c({}^{t}BuOH)_{T} \ge c(Ce^{IV})_{T}$, at 50 °C, the $\Delta c(Ce^{IV}) : \Delta c({}^{t}BuOH)$ ratio was determined. Completion of the reaction was indicated by the disappearance of the Ce^{IV} absorption band. The unreacted ${}^{t}BuOH$ was estimated by repeating the operation a number of times until the complete oxidation of ${}^{t}BuOH$ was achived. The average of five independent determinations of the above ratio was 3.98 \pm 0.10 and thus the stoichiometry conforms to:

$$4Ce^{4+} + (CH_3)_3COH + H_2O \rightarrow 4Ce^{3+} + CH_3COCH_3 + HCHO + 4H^+$$
(17)

The presence of both acetone and formaldehyde in the product mixture was confirmed via the Brady's test [27] by using NMR spectroscopy as follows. When the complete oxidation of *t*-BuOH was achieved (at 0.5 mol dm⁻³ HClO₄ and 50 °C) 1 g of 2,4 dinitrophenylhydrazine (Brady's reagent) was added on 10 ml of the solution. The yellow-orange solid that was obtained first it was washed and dried and then it was dissolved in DCCl₃. The NMR records of this solution gives a doublet centered at $\delta = 2.14$ and a singlet

at $\delta = 6.15$ which respectively confirms [28] the presence of acetone and formaldheyde in the product mixture.

In order to determine the possible formation of radicals the method employed by *Hassan* and *Rocek* [29] in the oxidation of alcohols by Cr^{VI} was used, substituing the acrylamide with acrylic acid. The process was repeated six times in which the acidty of the solvent and the concentrations of the Ce^{IV} and acrylic acid remained constant and the concentration of the reducer species, *t*-BuOH , was modified. The polimerisation of acrylic acid was confirmed by NMR spectroscopy. This indicates that free radicals are generated in the reaction mixture.

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