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Kinetic and Analytical Studies of Oxidation of Tannic Acid with Ammonium Hexanitratocerate(IV) in Nitric Acid Medium

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Kinetics of oxidation of tannic acid is extensively studied at various temperatures to evaluate the thermodynamic parameters and the formation constant (K_f) of the intermediate complex and furthermore to achieve the optimal conditions for analytical determination of tannic acid. In view of these facts the formation constant, K_f, and the other thermodynamic parameters evaluated in these investigations can be considered as a total measure of [Ce(IV)-glucose] complex, [Ce(IV)-gallic acid] complex and [Ce(IV)-unhydrolysed tannic acid] complex. Second order rate constants obtained in these investigations are utilised to correlate the effects of variation of [tannic acid], [Ce(IV)], [H^+], $a_{NO_3^-}$ and added [Ce(III)]. The mechanism of oxidation of tannic acid involves the formation of a transitory intermediate cyclic complex followed by disproportionation of the complex. The disproportionation of the intermediate complex is the rate determining step. The values for K_f, ΔE^*, $-\Delta H^*$, ΔF^*, ΔS^* and $\log A$ are found to be 2.456×10^4 lit mol^{-1}, 11.21 kcal $mole^{-1}$, 11.32 kcal $mole^{-1}$, –6.19 kcal $mole^{-1}$, –16.68 e.u. and 7.669 sec^{-1} respectively.

INTRODUCTION

Tannic acid finds very wide applications in different industries *viz.* as a clarification and stabilization agent in brewery, as an additive in food and flavouring industries, in pharmaceutical industries, in textile industries, in ink industries, in rubber and ceramic manufacturing industries and also in metallurgy as galvanoplastics and antirust products. A literature survey on the analytical estimations of such an industrially important compound, tannnic acid, shows that enough oxidimetric procedures have not been developed for an assay. Hence to assist in planning optimal analytical conditions in the cerimetric assay of tannic acid a kinetic study of the oxidation of tannic acid with ammonium hexanitratocerate(IV) in nitric acid medium was undertaken. This reagent is also advantageous as it is available in a high degree of purity and is stable for long periods. No previous studies are encountered in the literature regarding the kinetics of oxidation as well as analytical estimations of tannic acid by cerium(IV) in nitric acid medium. However, attempts on the analytical estimations of tannins and tannic acid based on the spectrophotometric or titrimetric or thin layer chromatography or high performance liquid chromatography are evident in the literature. Some of these methods are fraught with the difficulties of separation of gallic acid and tannic acid from natural products. The usual and most facile technique for analytical estimation of tannic acid is thin layer absorption chromatography on purified silica gel.

Fukui[1] attempted a correlation between *UV*-absorption spectra and the polarographic wave heights of aqueous solutions of five different tannins during ageing at 25°C. Hoefler[2] made a systematic study of the constituents of tea leaves, employing a reversed phase high performance liquid chromatography. Dzhindzholiya *et al.*[3] employed Sephadex column chromatographic technique for the separation of nine catechin polyphenol products in black tea infusion. Bagdasarova *et al.*[4] derived a formula for the relative tannin content at different stages and during twisting and fermentation of tea leaves in roller. A systematic analytical estimation of four different tannic acids of different origins employing HPLC technique was developed by Verzele and Delahaye[5, 6].

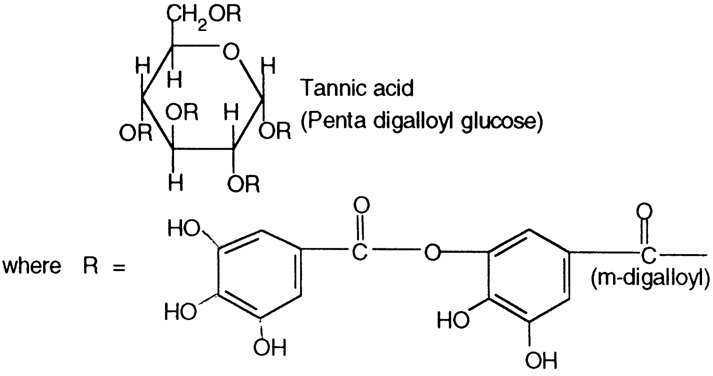
Zhaofan[7] developed a novel EDTA complexometric method for the rapid determination of tannin in *Rosa roxburghii* fruits. In this method the amount of EDTA consumed was directly converted to the tannin content. Heinrich[8] advanced a method for the analysis of tannin containing drugs and the method involves the estimation of total polyphenols through the reduction of molybdenum(VI).

Kobakhidze *et al.*[9] adopted Loewenthal's method of permanganometric estimation of tannins in Vietnam varieties of tea leaves. In the extraction and analysis of nucleic acid, starch and tannins from different plant materials Kedrowski[10] adopted the method of Swain and Goldstein[11] for the estimation of tannins. A quantitative determination of tannin in different materials through chromatographic method was described by Kemertelidze *et al.*[12]. Proctor[13] employed permanganate as an oxidant for the determination of tannins and tannic acid. A rapid method for the determination of tannins in barley grains by the extraction and complexation of flavanol with substituted cinnamaldehyde and further colorimetric estimation at 640 nm was developed by Truelsen[14]. A novel high frequency titrimetric method was adopted by Trubitsyna *et al.*[15] for the estimation of phenolic compounds of tannins and gallic acid in food stuffs. Nishizawa *et al.*[16] adopted the normal phase HPLC technique for the estimation as well as monitoring the degree of galloylation of gallotannin contents of the roots of *Paeonia lactiflora* commonly produced in Hokkaido in Japan.

It is evident from the foregoing literature survey that numerous efforts were made only on the exploration of nature, structure, composition of different types of tannins and development of different analytical methods involving spectrophotometric, HPLC and complexometric techniques. However, none has so far attempted the development of optimal conditions for the analytical estimations of tannins through cerium(IV) oxidimetric procedure in dilute nitric acid medium. Such a development obviously requires large scale experimental kinetic studies so as to establish optimal analytical conditions for the assay of such an industrially important vegetable material tannic acid/tannins through cerium(IV) oxidation. The authors are the first to carry out large scale experimental kinetic studies with cerium(IV) as an oxidant and establishing optimal analytical conditions for quantitative assay of tannic acid/tannins. Cerium(IV) species in nitric acid medium differ from those in $HClO_4$ and H_2SO_4 media and furhter much more complicated due to hydrolysis, dimerisation, complex formation with the nitrate ion and hydroxyl ion and association of cerium(IV) with cerium(III) as well as cerium(III)-nitrate association. However the oxidations of organic substrates with cerium(IV) in dilute nitric acid are facile and yield quantitative results with definite stoichiometries.

EXPERIMENTAL

The materials employed were of highest purity available (AR, E. Merck, G.R. grade or otherwise specified). A 0.1 N Ce(IV) solution was prepared in 1.0 N nitric acid and was further standardised by previously standardised Fe(II) solution. A stock 0.01 M tannic acid solution was prepared by dissolving a requsite amount of LOBA-CHEMIE Indoaustranal Co. G.R. grade tannic acid (m. wt. 1701) in conductivity water. Further this solution was standardised through known cerium(IV) sulphate as well as Proctor's modified Loewenthal permanganometric methods.[13] Stoichiometry of the reaction between cerium(IV) and tannic acid has been established for the experimental conditions employed as well as for 24, 48 and 72 hrs of the reaction. In every case it was found that one mole of tannic acid requires 192.0 equivalents of cerium(IV) for complete oxidation to formic acid and carbon dioxide, through the quinone and substituted quinone intermediate oxidation stages. The pattern of oxidation of tannic acid may be as follows.

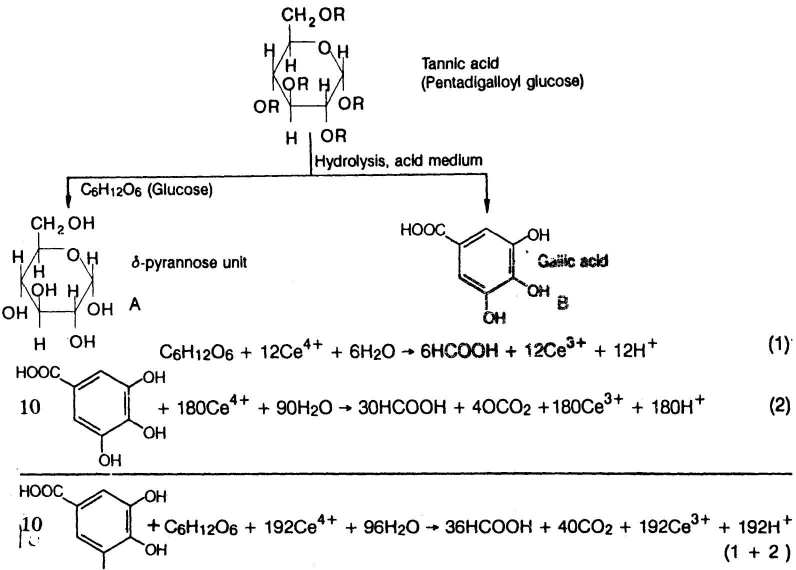


Tannic acid (Penta digalloyl glucose)

where R =

(m-digalloyl)

One of the the end-products, *viz.* formic acid, is less oxidised under the employed reaction conditions. The presence of this end-product formic acid was tested with (a) Tollen's reagent, (b) acidified potassium permanganate solution, and (c) freshly prepared mercuric chloride solution. All these tests have positively responded for the presence of formic acid in the above said reactions. For the convenience of establishing the above said stoichiometry, the hydrolysis of tannic acid into 10 moles of gallic acid and one mole of glucose is envisaged. Such type of hydrolysis of tannins/tannic acid into glucose and gallic acid or *meta*-gallic acid was also corroborated by Freudenberg[17].

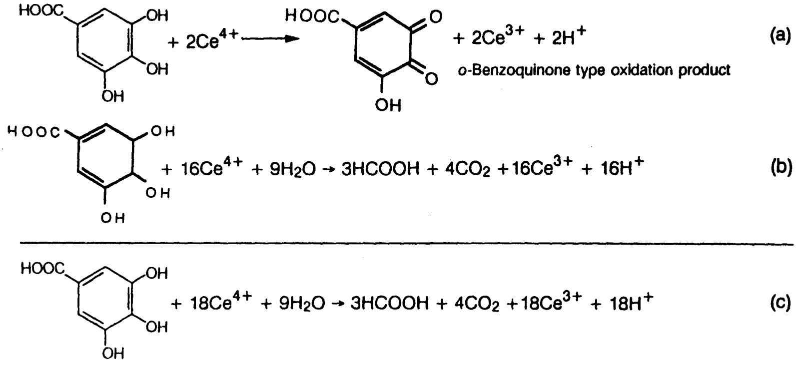


$C_6H_{12}O_6 + 12Ce^{4+} + 6H_2O \rightarrow 6HCOOH + 12Ce^{3+} + 12H^+$ (1)

$10\ (\text{gallic acid}) + 180Ce^{4+} + 90H_2O \rightarrow 30HCOOH + 40CO_2 + 180Ce^{3+} + 180H^+$ (2)

$10\ (\text{gallic acid}) + C_6H_{12}O_6 + 192Ce^{4+} + 96H_2O \rightarrow 36HCOOH + 40CO_2 + 192Ce^{3+} + 192H^+$ (1 + 2)

The probable pattern of oxidation of gallic acid may be as follows. Further, such *o*-benzoquinone type oxidation products are a common occurrence in the oxidation of catechols by cerium(IV)[7].



$+ 2Ce^{4+} \longrightarrow + 2Ce^{3+} + 2H^+$ (a)

$+ 16Ce^{4+} + 9H_2O \rightarrow 3HCOOH + 4CO_2 + 16Ce^{3+} + 16H^+$ (b)

$+ 18Ce^{4+} + 9H_2O \rightarrow 3HCOOH + 4CO_2 + 18Ce^{3+} + 18H^+$ (c)

The progress of reaction was followed by arresting the reaction mixture in a known excess of Fe(II) and back-titrating the unreacted Fe(II) with standard Ce(IV) sulphate (*ca* 0.01N) with ferroin as an indicator. For stoichiometrically equivalent concentrations of tannic acid and cerium (IV), the reaction follows simple second order kinetics. A plot of $1/(a - x)$ vs. time t is linear indicating the total order is two. At different [Ce(IV)] and [Tannic acid], the plot $2.303/(a - b) \log (a - x)/(b - x)$ vs. time t is also linear indicating first order dependence each in [Ce(IV)] and [Tannic acid]. As is observed in the linear plot, Fig. 1, ($1/k_2$ vs. 1/Tannic acid) the rate of oxidation increases with increase in [Tannic acid], under the experimental conditions, *viz.* [Ce(IV) = 1.92×10^{-2} M, [HNO_3] = 1.0 M at 35 ± 0.05°C. From the intercept and slope of this linear plot the stability constant of 1:1 intermediary complex has been evaluated at the above said conditions, $K_f = 2.456 \times 10^4$ litre mole^{-1} at 35 ± 0.05°C.

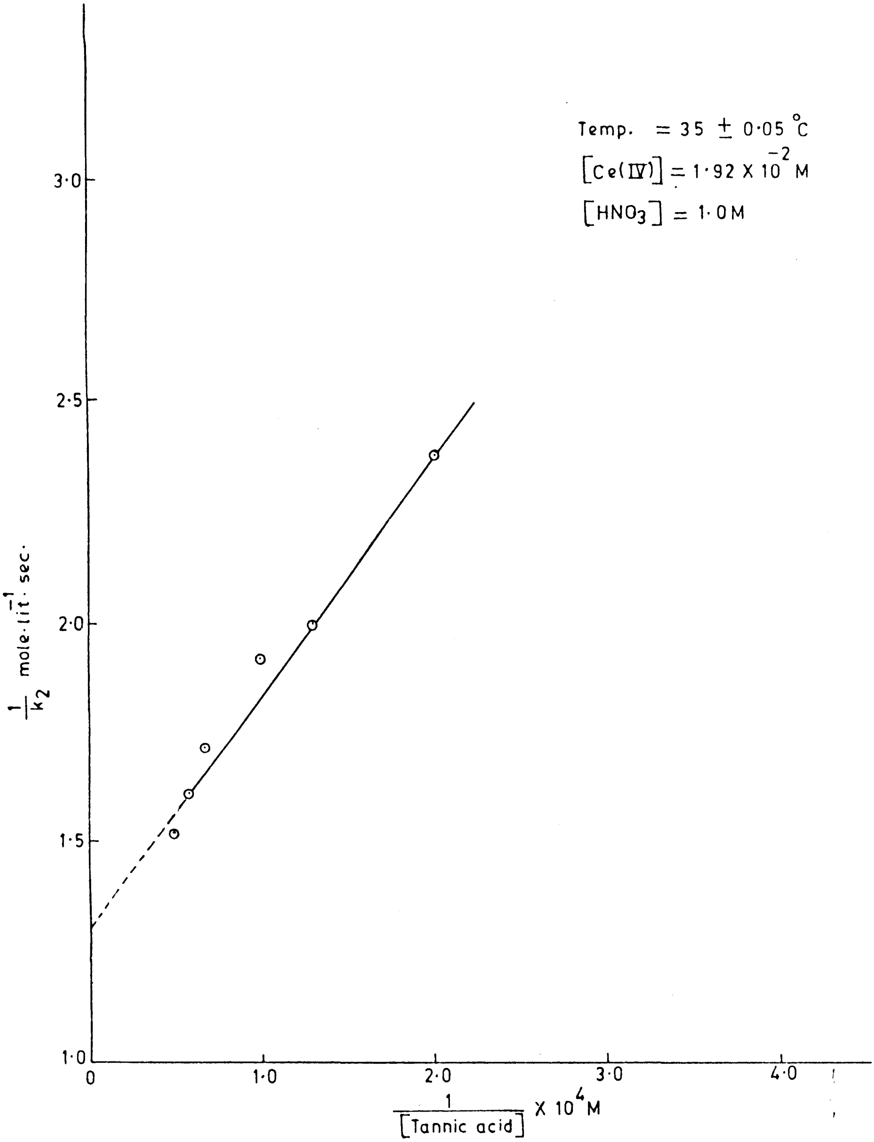
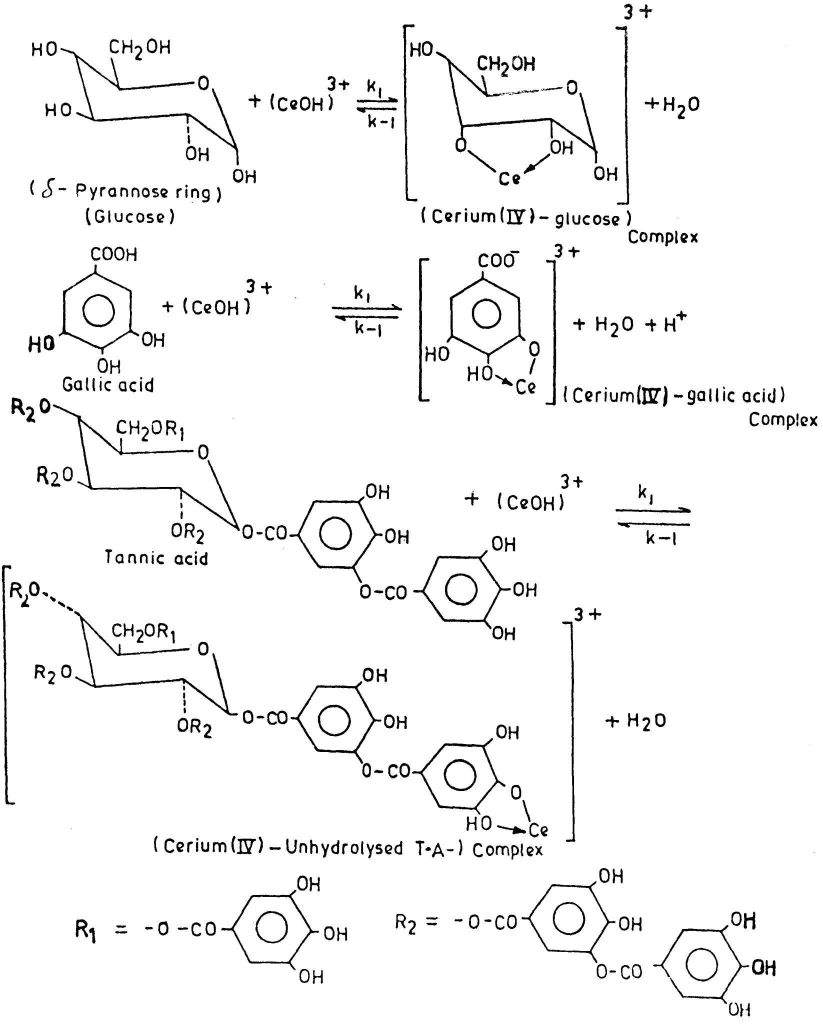


Fig. 1 Tannic acid—Ce(IV) reaction in 1 M nitric acid medium. Data of Fig. 1 plotted assuming A 1 : 1 tannic acid—Ce(IV) complex intermediate.

RESULTS AND DISCUSSION

The reaction involves the formation of prior complex between Ce(IV) and tannic acid which disproportionates by the second order type of kinetics. The tannic acid sample used here is a gallotannin and is mostly glucose ester of *meta*-digallic acid/gallic acid. According to Frudenberg[17] gallotannins are hydrolysable tannins and the hydrolytic products are glucose and gallic acid. In view of these facts the formation constant 'K_f' of the [Cerium(IV)–gallic acid] intermediary complex evaluated in these investigations can be considered as a total measure of the K_f values of [Cerium(IV)–glucose] complex, [Cerium(IV)–gallic acid] complex and [Cerium(IV)–unhydrolysed tannic acid] complex. The structures of the cyclic 1 : 1 intermediary complexes with respect to glucose, gallic acid and unhydrolysed tannic acid may be written as follows.



For stoichiometrically equivalent concentrations as well as higher concentrations of cerium(IV) and at constant tannic acid concentration, the rate of oxidation decreases with increase of [Ce(IV)] i.e. 52×10^{-2} M lit mole^{-1} sec^{-1} at 1.92×10^{-2} M [Ce(IV)] to 6.66×10^{-2} lit. mole^{-1} sec^{-1} at 7×10^{-2} M [Ce(IV)] at 35 ± 0.05°C, [HNO_3] = 1.0 M and [Tannic acid] = 1.0×10^{-4} M while the initial rate proportionately increases *i.e.* 5.25×10^{-3} mole lit^{-1}sec^{-1} at 1.92×10^{-2} M [Ce(IV)] to 22.39×10^{-3} mole lit^{-1} sec^{-1} at 7.0×10^{-2} M[Ce(IV)]. Such an accelerating effect in the initial rate may be due to the availability of kinetically reactive Ce(IV) species *viz.* $[Ce(OH)]^{3+}$ in the reaction mixture. In the study of effects of $[H^+]$ on the second order rate constant, vide Fig. 2, it is observed that the second order rate constant proportionately decreased with the dissociated $[H^+]$. This is in agreement with the observations of Duke and Forist[18]. The values

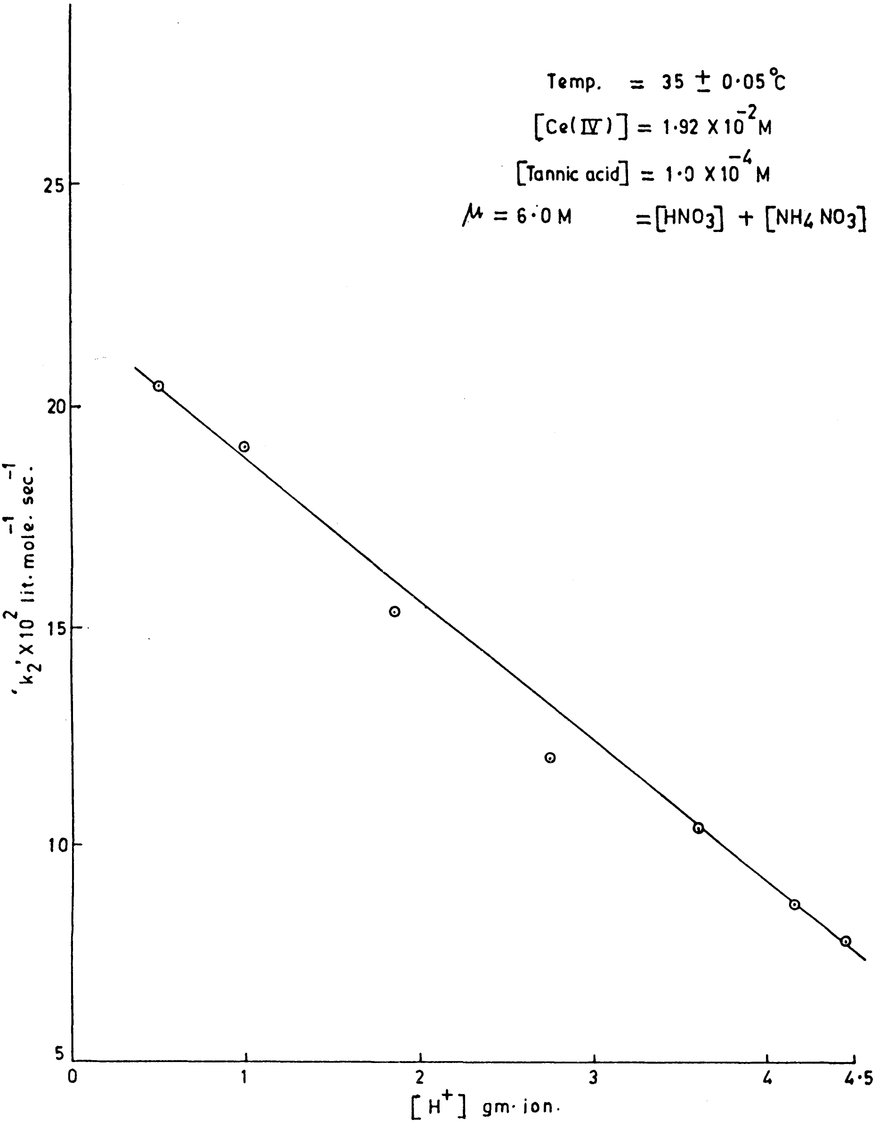


Fig. 2 Tannic acid—Ce(IV) reaction in nitric acid medium. Effect of dissociated $[H^+]$ on second order rate constant.

of $[H^+]$ at different concentrations of nitric acid were obtained from the spectroscopic data of RaO[19]. The rate of oxidation decreases proportionately with the activity of added NO_3^-. The added NO_3^- may complex with the reactive $[Ce(OH)]^{3+}$ species and converting it into less reactive species *viz.* $[Ce(OH^-)(NO_3)]^{2+}$ and $[Ce(OH^-)(NO_3)_2]^+$. Similar observations were also made by Shorter[20] in the oxidation of acetone by ceric ammonium nitrate. The activity data were taken from Landolt-Bornstein Tabellen Vol. III (1936).

The rate of oxidation of tannic acid is independent of the added cerous ions and this may be due to complexity of the molecular structure of tannic acid, *viz.* pentadigalloyl glucose and which may not facilitate the reactive $[CeOH]^{3+}$ species in any further association with cerium(III). The thermodynamic parameters recorded in these investigations are $\Delta E^* = 11.21$ kcal mole^{-1}, $-\Delta H^* = 11.32$ kcal mole^{-1}, $\Delta F^* = -6.19$ kcal mole^{-1}, $\Delta S^* = -16.68$ e.u. and frequency factor $A = 4.67 \times 10^7$ sec^{-1}. The values of ΔE^*, ΔS^* and log A recorded in these investigations corroborate the possibility of a C–C bond cleavage during the oxidation reactions.

Determination of tannic acid in a tannic acid sample by cerium(IV) in 0.5 N nitirc acid medium

Recommended Procedure: Transfer an aliquot of tannic acid solution (5.0–20 mg of tannic acid) to an Erlenmeyer flask provided with a leak-proof stopper. Add about 3.0–4.0 times excess of cerium(IV) nitrate solution required for complete oxidation, and add a requisite volume of 1.0 N nitric acid to maintain overall 0.5 N nitric acid concentration. From the present kinetic studies on the oxidation of tannic acid by cerium(IV) nitrate in nitric acid medium, it is quite obvious that the rate of oxidation of tannic acid is very much facilitated by lower concentrations of nitric acid (*ca.* 0.5 N). The mixture should be left out at room temperature (*ca.* 30°C) for atleast 50 minutes for complete oxidation to formic acid and carbon dioxide. The reagent blanks of cerium(IV) nitrate in 0.5N nitric acid under identical conditions showed no significant decrease in the concentration of cerium(IV). The above method constitutes a definite improvement over the Kapel and Karunanithy method[21] an other methods of assay cited in the foregoing literature.

A large number of determinations were carried out utilising the above stoichiometry at room temperature (*ca.* 30°C). As discussed earlier under stoichiometry, the number of equivalents of cerium(IV) consumed per mole of tannic acid oxidation are 192.0 and the end-products are formic acid and carbon dioxide. In all these analytical estimations the unused cerium(IV) was back-titrated with a standard iron(II) solution using ferroin as an indicator. Some representative analytical results are furnished in the following table. The factor worked out on the basis of the above said stoichiometry [1.0 Tannic acid : 192.0 Ce(IV)] is as follows.

1 ml of 0.1 N Cerium(IV) = 0.88606 mg of tannic acid.

TABLE 1

DETERMINATION OF TANNIC ACID IN TANNIC ACID SOLUTIONS BY AMMONIUM HEXANITRATOCERATE(IV) IN 0.5 NITRIC ACID MEDIUM AT ROOM TEMPERATURE (*ca.* 30°C)

Sr. No.	Tannic acid		Error %
	Taken (millimoles)	Found (millimoles)	
1.	0.0033	0.00327	−0.91
2.	0.0050	0.00498	−0.40
3.	0.0060	0.00603	+0.50
4.	0.0075	0.00758	+1.06
5.	0.0090	0.00905	+0.55
6.	0.0100	0.009914	−0.86
7.	0.0120	0.01197	−0.25

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