SHORT COMMUNICATIONS

KINETICS AND MECHANISM OF Ru(III) CHLORIDE-CATALYSED OXIDATION OF BENZALDEHYDE AND SUBSTITUTED BENZALDEHYDES BY TRICHLOROISO-CYANURIC ACID IN ACID MEDIUM

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OXIDATION of aromatic aldehydes using various oxidants has been reported earlier[1–10]. This note reports some studies on the Ru(III) catalysed oxidation of benzaldehyde and substituted benzaldehydes by trichloroisocyanuric acid (TCCA).

All the substrates were of analar (BDH) grade and were used after redistillation or recrystallization. The oxidant trichloroisocyanuric acid was of analar (Fluka) grade. The catalyst $RuCl_3$ was from Johnson Matthey (London) and its aqueous solution was standardized by the method of Horiuchi *et al*[11]. The progress of the reaction was monitored by estimating oxidant at regular intervals of time iodometrically. The experiments were carried out in duplicate to ensure reproducibility.

Oxidation of benzaldehyde and *m*–NO_2, *p*–Cl, *p*–OCH_3, *p*–CH_3, *p*–NO_2, *p*–Br by TCCA was carried out under identical conditions and the kinetic results can be summarized as follows.

(i) The reaction is zero order in TCCA and first order in substrate.
(ii) There is a first order dependence of the reaction on the catalyst Ru(III) chloride. The rate of the reaction is insensitive towards change in acid concentration in the range studied i.e. from 0.02 M to 0.2 M.
(iii) Added chloride ions accelerate the rate of reaction probably due to the formation of molecular chlorine as per the equilibrium.

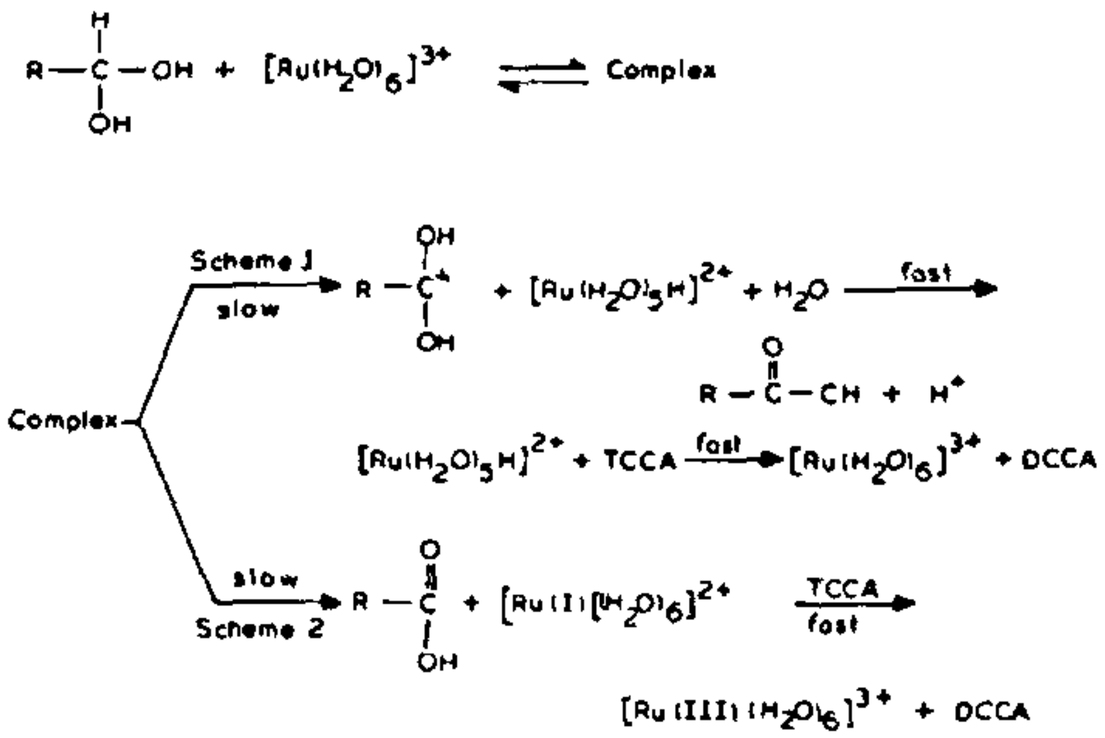
$$H_2OCl^+ + Cl^- \rightleftharpoons Cl_2 + H_2O$$

(H_2OCl^+ is the species liberated by the hydrolysis of TCCA).
(iv) Increase in acetic acid from 10 to 50% (other conditions being the same) decreases the rate constant.

The order of reactivity of different substituted aldehydes is

p–OCH_3 > *p*–CH_3 > *p*–NO_2 > *m*–NO_2 > benzaldehyde > *p*-Cl > *p*-bromo benzaldehyde.

The plot of $\log k_1$ versus σ values is concave indicating that electron releasing groups enhance the reaction rate and electron-withdrawing groups retard the rate except in *p*-nitro benzaldehyde and *m*-nitro benzaldehyde. Such abnormality has earlier been observed[12–14] in the catalysed oxidation of benzaldehydes and benzyl alcohols. It appears that the substrates having electron-releasing groups react with rate-determining step of hydride ion loss which is supported by the high negative value of $\rho = -2.5$. In such cases a mechanistic pathway involving an outersphere complex might be operating (scheme 1).



Scheme 1.

But in the case of substrates having electron-withdrawing group, the reaction probably proceeds through an inner-sphere complex (scheme 2) involving a rate determining proton loss.

Such complexes can break down in two ways i.e. either by proton loss or by hydride ion transfer in a slow step. The loss of proton is associated with an inner sphere mechanism involving changes in the valence state of ruthenium which is finally reconverted to ruthenium(III) by TCCA in a fast step.

In the outer sphere mechanism as suggested for electron-releasing group substrates, the reaction proceeds with a rate-limiting hydride ion loss without change in valence of Ru(III) species and the resulting hydride complex breaks down in a fast reaction with TCCA. Then in both the pathways zero order dependence on [TCCA] is observed.

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PACHYTENE CHROMOSOMES OF COLEUS FORSKOHLII

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COLEUS FORSKOHLII Briq. (family Lamiaceae) is an important source of Coleonol (Forskolin) which is being developed as a drug for glaucoma, congestive cardiomyopathy and asthma[1–4]. Its somatic chromosomes are relatively small and lack discernible morphological markers for identification. On the other hand at pachytene stage of meiotic prophase, where the chromosomes are paired in an extended condition, each pair is identifiable by distinct morphological features. Detailed pachytene analysis of the chromosome complement in this species is of considerable importance as it will help in understanding the evolutionary relationship and preparing the linkage groups for use in genetic and cytogenetic investigations. The present communication reports on the morphology of 15 chromosome pairs in *C. forskohlii*. This is, as far as we know, the first report presenting complete pachytene analysis in this species.

The young flower buds from a healthy plant of *C. forskohlii* were fixed in a freshly prepared acetic-alcohol mixture (1:3) for 24 h. The anthers were stained and squashed in 2% acetocarmine. For all measurements and the study of morphological details five intact cells at mid-pachytene stage in which all the 15 bivalents could be traced from one end to the other were selected from temporary slides. The chromosomes were numbered one to fifteen following the method adopted by McClintok[5]. For describing the position of centromeres on the chromosome, the method of Leven *et al*[6] was followed.

At pachytene, the chromosome complement resolved itself into a haploid set of 15 bivalents. All the chromosomes were differentiated into euchromatic and heterochromatic regions along their lengths. The centromeres were located within the heterochromatic regions and the chromosome ends were rarely terminated by a prominent telomere. The mean observations relating to the characteristic features of the chromosome identified as 1 to 15 are summarized in table 1. The photomicrographs of a single cell showing the entire pachytene chromosome complement and its interpretive drawing are shown in figures 1 and 2 respectively. The *C. forskohlii* karyotype with distinguishing features of each chromosome is shown in figure 3.

The length of the haploid complement was measured at 515.88 μ. The chromosome length varied between 50.45 μ and 15.00 μ and the arm ratio between 0.09 and 0.90. The chromosomes were comprised of largely euchromatic regions (EUL: HCL = 1:0.286). The variation in arm ratio demonstrates that the chromosomes of *C. forskohlii* are acrocentric to metacentric (table 1).

Chromosomes 9 and 13 are the nucleolus organizing chromosomes which could be readily identified by virtue of their constant association with the nucleolus and presence of nucleolus organizing region in their short arms which unlike rest of the chromosomes were totally heterochromatic. In addition to length, centromere position and extent of differentiation into euchromatic and heterochromatic regions, size, number and position of chromomeres formed the diagnostic criteria on the basis of which the 15 chromosomes of *C. forskohlii* could be identified at pachytene.