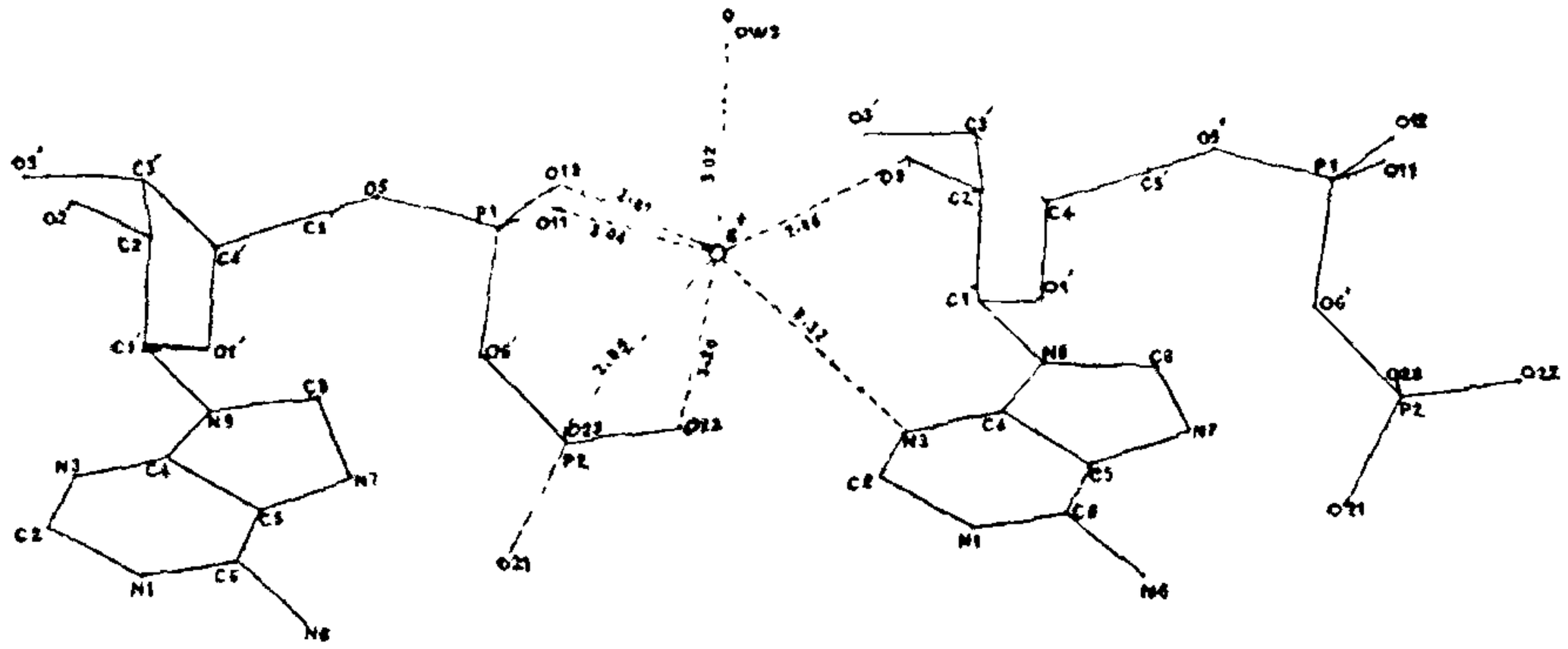

FIG. 2. View of the coordination sphere of potassium ion down *c*-axis (O11 bound to potassium belongs to the *c*-cell translated ADP molecule).

and that about C5′–O5′ bond is trans(C4′–C5′–O5′–P1 = 144·6°). The pyrophosphate moiety has a staggered geometry. K^+ ion is in contact with three *independent* ADP *molecules. Its coordination sphere* consists of seven nearest neighbours with distances ranging from 2·8 Å to 3·3 Å as shown in the diagram (Fig. 2). In the extended crystal structure there is no self-association of bases either by base pairing or by base stacking. The main interactions between different molecules are pairs of hydrogen bonds between the adenine base and the pyrophosphate groups (Fig. 3). *Similar interactions have been observed in* ADP–free acid[2] and ADP–Rb structures also. The water molecules stabilise the structure by forming hydrogen bonds between two neighbouring molecules of ADP–K related by a two-fold axis.

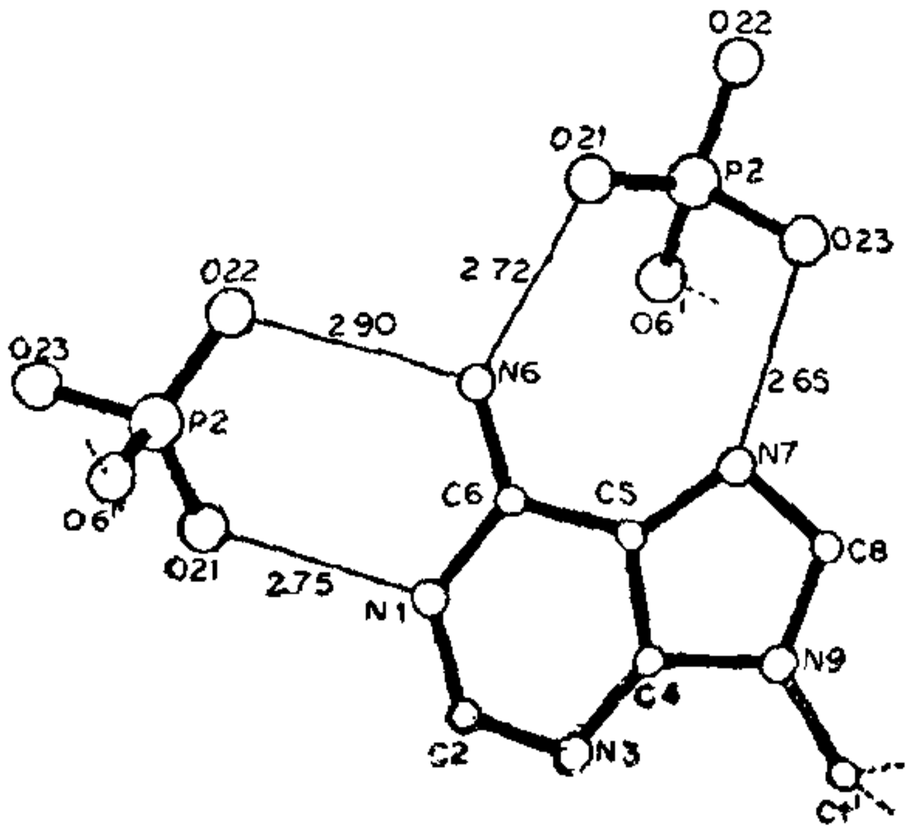

FIG. 3. Hydrogen bonds between base and pyrophosphates.

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Department of Physics and
ICMR Centre on Genetics and
Cell Biology,
Indian Institute of Science,
Bangalore 560012, India,
August 13, 1979.

S. K. KATTI.
M. A. VISWAMITRA.

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KINETICS AND MECHANISM OF Ru(III) CATALYSED OXIDATION OF ALCOHOLS BY PERIODATE

TRANSITION metal complexes are known to act as good hydride ion abstracting agents both in acidic[1] as well as in basic[2] media. Under normal conditions monohydric alcohols do not undergo oxidation by periodate. It was therefore thought worthwhile to find out whether Ru(III) salts can act as catalysts in the oxidation of simple monohydric alcohols by periodate in basic medium.

All the chemicals used were of (BDH) AR grade or extra pure quality and purified by standard methods wherever necessary. A known volume of alcohol was added to the flask containing the required quantities of NaOH, $RuCl_3$ and $NaIO_4$ solutions after thermostating them for 30 min. Unreacted periodate at

TABLE I

Dependance of rate on [periodate] and [cyclohexanol] $[Ru(III)] = 1{\cdot}33 \times 10^{-6}\,M$; $[NaOH] = 0{\cdot}01\,M$; $T = 303°K$

[Periodate] × 10^3 mol. lit^{-1}	[cyclohexanol] × 10^2 mol. lit^{-1}	$k_o \times 10^5$ mol. lit^{-1} min^{-1}	k_o/[cyclohexanol] × 10^3 min^{-1}
0·800	2·00	1·62	..
1·00	2·00	1·43	..
2·00	2·00	1·50	..
3·00	2·00	1·47	..
4·00	2· 0	1·39	..
2·00	1·00	0·690	0·690
2·00	2·00	1·50	0·750
2·00	3·00	2·28	0·760
2·00	4·00	2·94	0·735
2·00	5·00	3·69	0·738
2·00	6·00	4·30	0·717

TABLE II

Dependance of rate on [Ru(III)] and $[OH^-]$ *[periodate]* $= 2{\cdot}00 \times 10^{-3}\,M$; *[cyclohexanol]* $= 2{\cdot}00 \times 10^{-2}\,M$; $T = 303°\,K$

$[RuCl_3] \times 10^6$ mol. lit^{-1}	$[OH^-] \times 10^2$ mol. lit^{-1}	$k_o \times 10^5$ mol. lit^{-1} min^{-1}	$k_o/[RuCl_3]$ min^{-1}	$k_o/[OH^-]^2 \times 10$ lit. mol^{-1} min^{-1}
0·442	0 010	0·530	0·120	..
0·884	0·010	0·980	0·111	..
1·33	0·010	1·50	0·113	..
1·77	0·010	1·88	0·106	..
2·21	0·010	2·74	0·124	..
1·33	0·250	0·100	..	1·61
1·33	0·750	0·880	..	1·56
1·33	1·00	1·50	..	1·50
1·33	1·50	3·30	..	1·47
1·33	2·50	8·29	..	1·33

definite intervals was estimated iodometrically[3]. The product of oxidation was identified as the corresponding aldehyde or ketone from their characteristic spot tests[4]. The melting points of the 2 : 4—DNP derivatives of the products, *viz.*, acetaldehyde, acetone and cyclohexanone obtained in the oxidation of *n*-propanol, isopropanol and cyclohexanol were found to be 166, 131, 161° C respectively, in close agreement with the standard values[6]. Stoichiometric studies using high concentrations of periodate revealed that one mole of alcohol required one mole of periodate to form one mole of the carbonyl compound.

Under the conditions, [alcohol] $\gg$ [periodate] the rate of oxidation was found to be independent of initial concentration of periodate (Table I), exhibiting zero order kinetics in [periodate]. The order in [alcohol] and [Ru(III)] were found to be one each as can be seen from Tables I and II respectively. The k_o values (where k_o is the zero order rate constant) increased with increase in $[OH^-]$ and a near second order ($\sim 1{\cdot}84$) dependance in $[OH^-]$ was obtained (Table II). This might probably be due to the formation of a complex between one mole of Ru(III) and two moles of hydroxide ion. Addition of salts

such as NaCl and KCl had negligible effect on the rate.

$RuCl_3$ in aqueous solution is known to exist as[6,2] $[Ru(H_2O)_6]^{3+}$ or $[Ru(H_2O)_{6-x}(OH)_x]^{3-x}$ depending upon the conditions of pH (where x is always less than six[7]). If the latter type of the complex is to be the reactive species the rate of oxidation should increase with an increase of $[OH^-]$ which infact was observed in the present study. Since there was negligible effect to salts on the rate of oxidation, one could expect the reaction to be an ion-dipole type. In view of the above facts, the following mechanism involving hydride ion transfer from alcohol moity to ruthenium(III) has been suggested to explain the kinetic data.

TABLE III

Effect of temperature on rate

Substrate	$k_1 = \frac{k_0}{[\text{alcohol}]} \times 10^3$ sec^{-1}		
	283° K	293° K	303° K
Cyclopentanol	1·08	1·29	1·53
Cyclohexanol	1·15	1·20	1·25
Cycloheptanol	1·43	1·29	1·17
n-propanol	2·80	3·55	4·43
iso-propanol	0·224	0·302	0·400
t-butanol	no reaction	no reaction	no reaction

SCHEME 1

$$[Ru(H_2O)_6]^{3+} + OH^- \overset{K_1}{\rightleftharpoons} [Ru(H_2O)_5OH]^{2+} + H_2O \quad (1)$$

$$[Ru(H_2O)_5OH]^{2+} + OH^- \overset{K_2}{\rightleftharpoons} [Ru(H_2O)_4(OH)_2]^{1+} + H_2O \quad (2)$$

$$[Ru(H_2O)_4(OH)_2]^{1+} + R\text{—}\underset{}{\overset{R'}{\underset{|}{C}}}HOH \overset{K_3}{\rightleftharpoons} \left\{ R\text{—}\overset{R'}{\underset{H}{C}}\text{—}O\text{—}H \;\; [Ru(H_2O)_4(OH)_2]^{1+} \right\} \quad (3)$$

(complex)

$$\text{Complex} \xrightarrow[\text{slow}]{k} R\text{—}\overset{R'}{\underset{|}{C}}{=}O + [Ru(H_2O)_5OH] + H^+ \quad (4)$$

$$[Ru(H_2O)_5(OH)] + IO_4^- \xrightarrow{\text{fast}} [Ru(H_2O)_4(OH)_2]^{1+} + IO_3^- + OH^- \quad (5)$$

From eqns. 1, 2, 3 and 4, the rate expression comes out to be

$$-d\frac{[IO_4^-]}{dt} = k_0 = \frac{k K_1 K_2 K_3 [\text{alcohol}] [Ru(III)] [OH^-]^2}{\{1 + K_1[OH^-]\}\{1 + K_2[OH^-]\}\{1 + K_3[\text{alcohol}]\}} \quad (6)$$

Since kinetically no complex formation could be detected either with substrate or catalyst, the values of K_1, K_2 and K_3 might be assumed to be very low. The Eqn. (6) reduces to

$$-d\frac{[IO_4^-]}{dt} = k K_1 K_2 K_3 [\text{alcohol}] [Ru(III)] [OH^-]^2 \quad (7)$$

which substantiates the results obtained.

The order of reactivity of the acyclic alcohols was found to be *n*-propanol > iso-propanol > tert-butanol. Since no α-CH bonds are present in case of tert-butanol, it was unaffected by periodate in the presence of ruthenium. The lower rate of oxidation of isopropanol compared to *n*-propanol could be due to steric factors overweighing the inductive effects at α-carbon atom during the transfer of hydride ion to the metal complex. The different structural conformations might be responsible for the variation of trend in rates in the case of cyclanols. In the higher temperature range the rates were found to decrease with increase in temperature for all the alcohols studied. This trend has been observed in the case of cycloheptanol even at the low temperatures studied (10–30° C). This could be

probably due to the exothermicity of the equilibria (1) and (2).

Department of Chemistry, Osmania University, Hyderabad 500 007 (A.P.), *February* 12, 1979.

M. PRASADA RAO.
B. SETHURAM.
T. NAVANEETH RAO.

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A NOTE ON NATURAL CROSSING BETWEEN *CASSIA ACUTIFOLIA* DELILE AND *CASSIA ANGUSTIFOLIA* VAHL AND THEIR GENETIC RELATIONSHIP

THE genus *Cassia* Linn. belongs to the family Leguminosae, sub-family Papillionaceae and comprises about 340 spp.[1]. Taxonomically *Cassia acutifolia* Delile and *C. angustifolia* Vahl are very closely related, differing from each other in pod and leaf dimensions. The leaves and pods of both possess purgatory properties and have an important place in medicine. The crude drug is used in indigenous and Unani systems of medicine, while in recent years the manufacture of glycosidal preparations from the leaves and pods has also been undertaken.

In October, 1975, a few seeds of *C. acutifolia*, introduced from Sudan, were sown in a plot adjacent to a plot sown a few days earlier with *C. angustifolia*. The seeds were sown in plots 30 × 45 cm and the distance between two plots was 60 cm. Plants in both the species were homogeneous. In the next season, composite seeds of *C. acutifolia* were sown and slight variations in pod shape were observed. However, in the succeeding generation, the author came across a large number of plants showing considerable variations in pod characters from those of *C. acutifolia*. These plants were therefore presumed to be the F_2 generation, resulting from natural crossing between the two species, as no other *Cassia* or any related species was growing in the neighbourhood. Some quantitative characters of parents and F_2 are given in Table I.

Thus, in this hybrid population there is a wide variation in size, shape and weight of pods and the number of pods per plant and rachis. All the plants were fertile.

The chromsoome number in *C. angustifolia* has been found to be $n = 14$ thus confirming the earlier report[2]. Similarly in *C. acutifolia* the author observed the chromosome number to be $n = 14$. Meiosis in both the species was regular with fourteen bivalents, and no irregularities could be noticed. Chromosome distribution was normal, leading to tetrad formation. The pollen fertility was 98% and seed germination percentage was 90. Meiotic chromosome behaviour of plants in F_2 generation also showed regular pairing of chromosomes leading to the formation of 95–98% fertile pollen and 88–90% fertile seed, indicating very close affinity between genomes of the two species.

Thus, the morphological similarity of *C. acutifolia* and *C. angustifolia*, their crossability, viable segregation and regular meiotic chromosome behaviour show clearly that the two species are very closely related, and slight morphological variations in these species might be due to small gene mutations. Further studies to confirm the above findings are in progress.

TABLE I

Some quantitative characters of pods of Cassia acutifolia, C. angustifoia *and their F_2 generation*

Character	*C. acutifolia* 15*		*C. angustifolia* 15*		F_2 Generation 22*	
	Range	Mean SE	Range	Mean SE	Range	Mean SE
No. of pods per receme	8–12	10 ± 0·4	8–12	9 ± 0·3	10 29	16 ± 1·9
Length of pod	3·2–5·0	4·2 ± 0·2	3·0–5·1	4·3 ± 0·5	2·8 6·8	4 6 ± 2·6
Breadth of pod	1·5–2·4	2·2 ± 1·0	1·3–1·8	1·5 ± 0·9	1·2 2·4	1·9 ± 2·1
No. of pods per plant	365–640	488 ± 18·5	342–580	412 ± 22·3	171–1848	848 ± 91·0
Weight of pods per plants (g)	69–132	102 ± 17·7	61–116	88 ± 15·7	35–591	212 ± 59 0
Weight of 100 pods (g)	19–22	21 ± 0·3	18 20	19 ± 0·3	10 32	25 ± 2·9

* No. of plants observed.