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INTERACTION OF RHODIUM(III) WITH NUCLEIC ACIDS

SINCE the report of Rosenberg *et al.*[1,2] that certain platinum group metals have anti-tumor and anti-viral activities considerable interest has developed in recent years on the study of metals in biological systems. Rhodium is one of the metals found to be anti-tumor in character but hardly any work is reported about its interaction with DNA although there is a strong background that its effectiveness as a drug is based on the DNA level[3,4]. The present communication is aimed to fill in the lacuna.

Calf thymus DNA was obtained from Swarch Bioresearch Inc., and was used without further purification. DNA was dissolved by adding small amounts of a mixture of acetate buffer pH 5·0 (0·01 M) and $NaClO_4$ (0·01 M) to DNA at intervals of 3–4 hours for 2–3 days at 4° C with occasional gentle stirring. The stock solution was diluted to the desired concentration before use. Analar $RhCl_3 \cdot H_2O$ and analar $NaClO_4$ were obtained from Johnson Matheys Chemicals Ltd., (London) and E. Merck, Germany respectively. Spectral studies were carried out in a Beckmann spectrophotometer Model 25. For melting temperature studies, UNICAM SP700 Spectrophotometer with accessories SP770 and SP775 were used. Viscosity measurements were carried out at 30° C using Ubbelhode viscometer.

All the spectral and viscosity measurements were carried out in acetate buffer (0·01 M) at pH 5 containing 0·01 M $NaClO_4$ · Rh(III) Cl in aqueous solution is a well studied system[5,6] and all the species of the system are identified. The major species in acetate buffer containing 0·01 M $NaClO_4$ were found to be *cis* and *trans* $RhCl_3(H_2O)_3$ and $RhCl_2(H_2O)_4^+$, and are in accordance with those reported in literature.

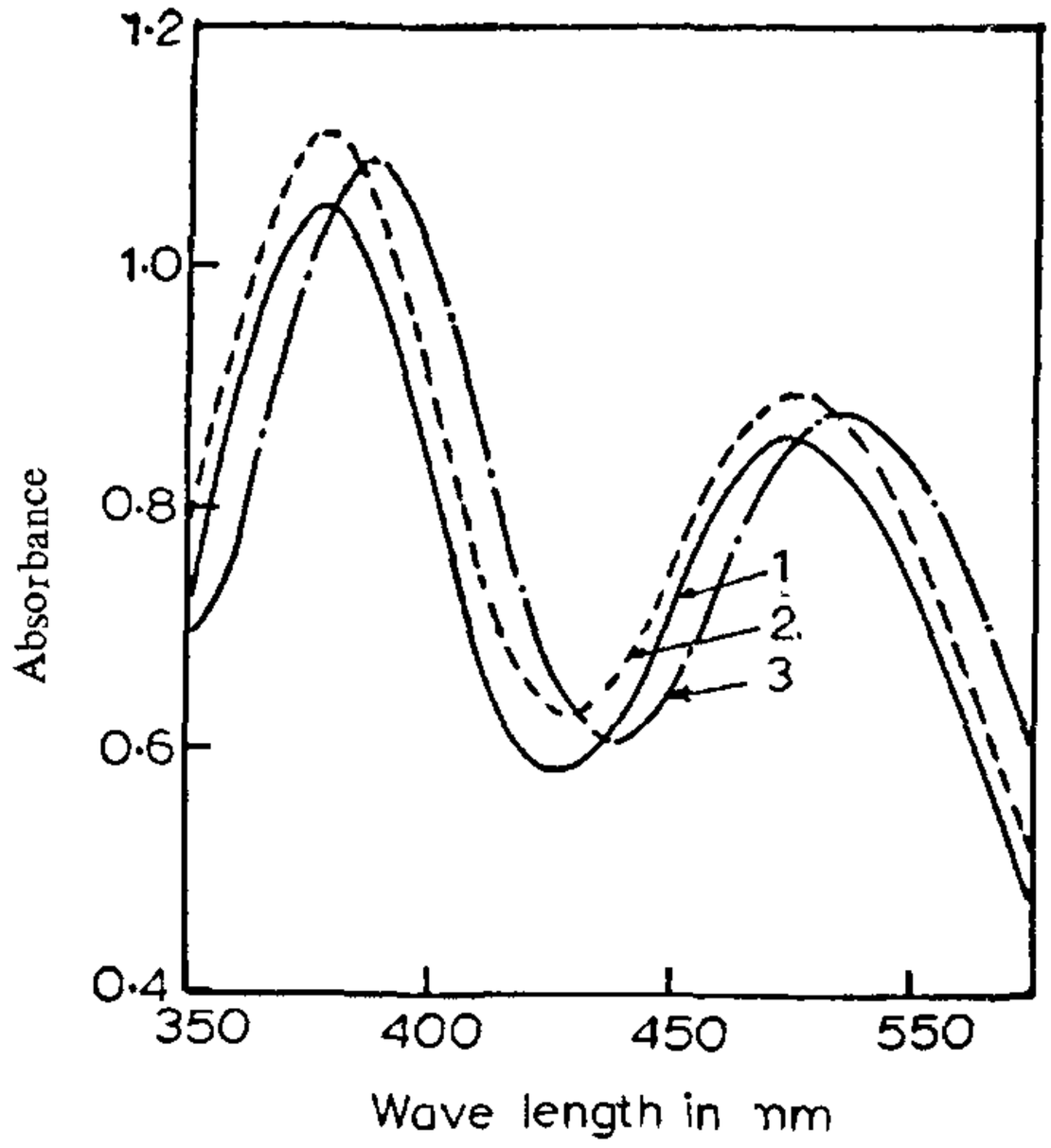

FIG. 1. Effect of DNA on the visible spectra of $RhCl_3$ concentration of DNA = $1·074 \times 10^{-4}$ M (P). Acetate buffer 0·01 MpH 5 in 0·01 M $NaClO_4$. 1. $RhCl_3$ alone, 2. $RhCl_3$ with DNA $r = 13·91$, 3. $RhCl_3$ with DNA $r = 9·1$.

$RhCl_3$ was found to interact with the DNA but compared to other metals (Hg, Au, Cu, Pd)[7–11], the interaction is very slow at room temperature. The interaction was studied at 37° C and takes about 96 hours to attain equilibrium. Both the visible spectra of Rh(III) as well as the u.v. spectra of DNA are affected. The peaks at 380 nm and 475 nm for Rh(III) were shifted to 395 nm and 490 nm respectively on addition of DNA ($r = 13·91$). The DNA peak at 258 nm was shifted to 272 nm on addition of Rh(III) ($r = 2·5$), the extent of the shift depending on the r value

$$\left(r = \frac{\text{Concentration of Rh(III) in Moles/litre}}{\text{Concentration of DNA Moles/litre in terms of phosphate}}\right).$$

This probably indicates that Rh(III) interacts with the base moieties of the DNA since they constitute the chromophore of the DNA molecule. The viscosity of DNA upon addition of Rh(III) decreases considerably with time, reaching a constant value after 72 hours. The extent of this decrease is a function of r values and is assymptotic in nature. The viscosity change is similar to that observed for Pd(II)-DNA[10] and

TABLE I

Effect of Rh(III) on the viscosity of Calf thymus DNA at pH = 5 in acetate buffer 0·01 M Containing 0·01 M $NaClO_4$ at 30° C. Concn. of DNA = 1·459 × 10^{-4} M (P) η_{sp} of DNA = 0·1310

Sl. No.	Concn. of Rh(III) M/l	*r* value	Specific viscosity η_{sp}					
			0 hr.	6 hrs.	12 hrs.	48 hrs.	72 hrs.	96 hrs.
1.	5·150 × 10^{-5}	0·36	0·1310	0·1266	0·0934	0·0803	0·0699	0 0486
2.	1·075 × 10^{-4}	0·72	0·1310	0·1196	0·0829	0·0672	0·0487	0 0410
3.	2·150 × 10^{-4}	1·44	0·1290	0·1170	0·0637	0 0484	0·0436	0·0349
4.	3·225 × 10^{-4}	2·16	0·1266	0·1190	0·0611	0·0398	0·0394	0·0305

TABLE II

U.V. Spectral Characteristics of Native Calf thymus DNA—(Rh(III) System at pH 5 in Acetate buffer (0 01 M) containing 0·01 M $NaClO_4$ after reaching equilibrium. Concn. of DNA = 1·4328 × 10^{-4} M/l

Sl. No.	Concn. of DNA Moles/litre	Concn. of Metal in Moles/litre	*r* values	λ_{max}	O.D. at λ_{max}
1.	1·4328 × 10^{-4}	—	—	258 nm	0·84
2.	,,	2·1 × 10^{-5}	0·09	260·5 nm	0·88
3.	,,	5·3 × 10^{-5}	0·36	262 nm	0·95
4.	,,	1·07 × 10^{-4}	0·90	266 nm	0·96
5.	,,	1·93 × 10^{-4}	1·80	268 nm	0·97
6.	,,	2·68 × 10^{-4}	3·16	272 nm	0 98

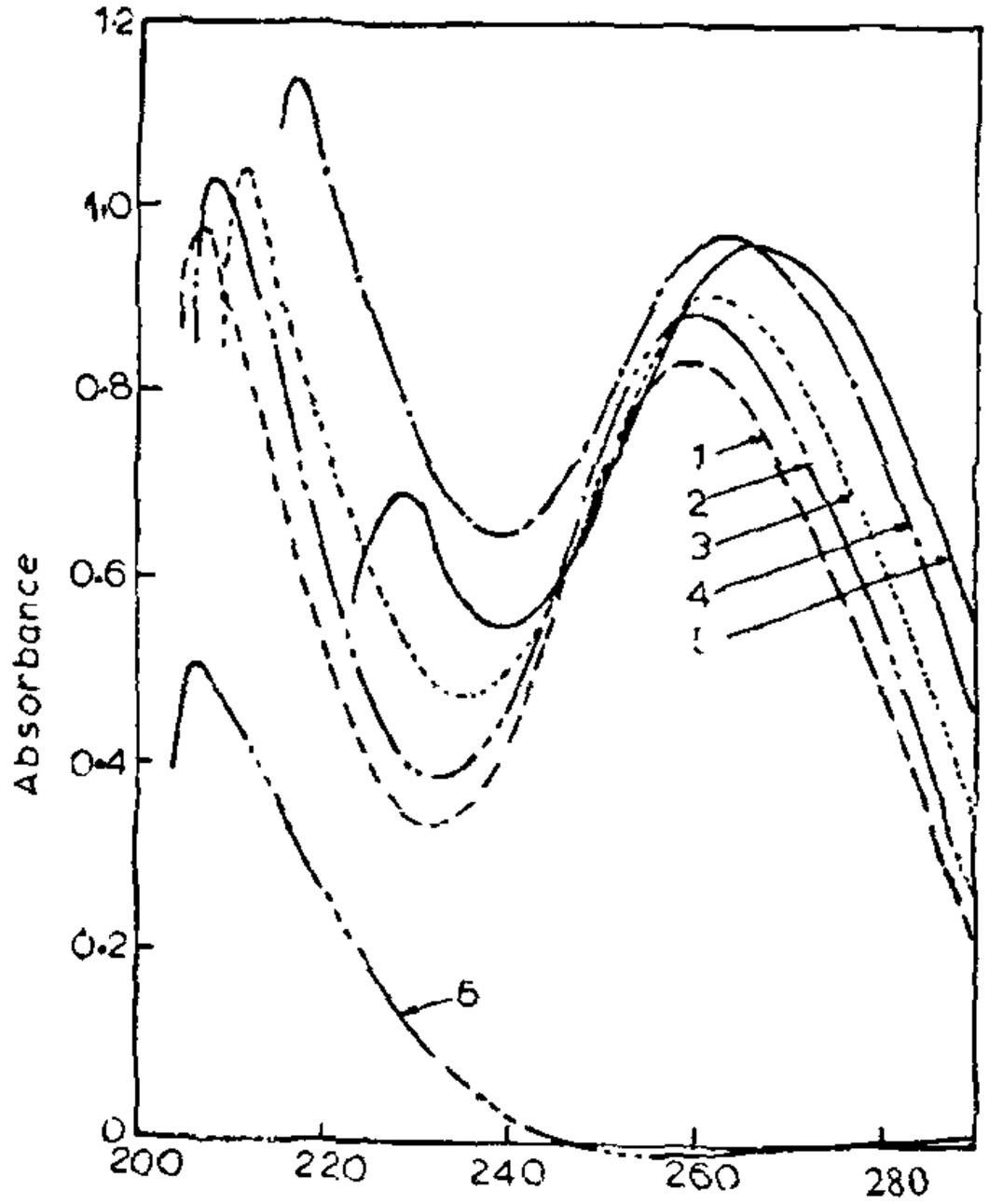

FIG. 2. Effect of $RhCl_3$ on UV spectra on DNA after reaching equilibrium concentration of DNA 1·477 × 10^{-4} M(P). Acetate buffer pH 5 (0·01 M) in 0·01 M $NaClO_4$.

1. DNA alone, 2. $r = 0·09$, 3. $r = 0·9$, 4. $r = 1·8$, 5. $r = 2·2$, 6. $RhCl_3$ alone.

Au(III)-DNA[9] systems. At low ionic strength (0·01 M $NaClO_4$) the melting temperature of DNA increases at low values of *r* (0–0·4) but decreases at higher *r* values (0·4 upwards). At high ionic strength (0·2 M $NaClO_4$) the melting temperature profile shows decrease for all values of *r*. These results seem to suggest that Rh(III) binds both to phosphate and the bases like Cu or Au[8,9]. Further detailed studies are in progress.

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KINETICS OF Ru^{3+} CATALYSED OXIDATION OF PROPANOL ETHYLENEGLYCOL AND MANNITOL BY CERIC SULPHATE

THE use of various catalysts like Ag^{+} (ref. 1), Mn^{2+} (ref. 2), Cu^{2+} (ref. 3) and Hg^{2+} (ref. 4) have been reported in the oxidation of different organic compounds by ceric sulphate. In all these cases the catalytic activity was found only when the catalysts concentration was as high as 10^{-2} M. In this paper the kinetic data on the oxidation of *n*-propanol, isopropanol, ethyleneglycol and mannitol by Ce^{4+}, catalysed by Ru^{3+}, wherein the concentration of catalyst is as low as 10^{-6} M, are presented. The use of platinum group metals like Ru^{3+} in trace amounts as cataslyts in homogeneous reactions *involving organic substrates* and Ce^{4+} *is a new* feature of this study.

All chemicals used were of BDH (AR) grade and Ru^{3+} used was a *Johnson-Matthey sample. The* concentration of Ru^{3+} was estimated by chelatometric titration using excess of EDTA and back titrating the excess with Bi^{3+} using xylenol orange *indicator*[5]. The rate of the reaction was followed by estimating the unreacted Ce^{4+} at different time intervals by quenching the aliquots of the reaction mixture in known excess of ferrous ammonium sulphate and titrating the unreacted ferrous against standard ceric sulphate using ferroin as indicator. The initial rate method was followed for calculating the order of reaction. The oxidation of iso-propyl alcohol yields acetone, *n*-propyl alcohol yields propionaldehyde, ethylene-glycol yields formaldehyde, mannitol yields mannose, which were identified by characteristic spot tests[6].

It is now fairly well established that ceric ion oxidises the alcohols *via* the formation of free radicals[7]. The mechanism of the uncatalysed reaction could be represented by the following scheme taking *mannitol* as a typical case.

$$Ce^{4+} + C_6H_{14}O_6 \xrightarrow{\text{slow}} Ce^{3+} + \dot{C}_6H_{13}O_6 + H^{+}$$

$$Ce^{4+} + \dot{C}_6H_{13}O_6 \xrightarrow{\text{fast}} Ce^{3+} + M_1 + H^{+}$$

M_1 = first stage oxidation product mannose.

At constant $[H^{+}]$ the above *mechanism gives a rate* law:

$$\frac{-d[Ce^{4+}]}{dt} = k''[Ce^{4+}][C_6H_{14}O_6]$$

which satisfies the kinetic data, *viz.*, order one with respect to (mannitol) and (Ce^{4+}). The formation of free radicals was detected by induced polymerisation of acrylamide. Similar mechanism was proposed *for n-propanol*, isopropanol and ethyleneglycol in the uncatalysed reaction.

In the Ru^{3+} catalysed reaction the order of $[Ce^{4+}]$ was *found to be one as observed from the linear plot* of $\log a/a - x$ *vs.* time when $(Ce^{4+}) \ll$ [alcohol]. This was true with all the alcohols studied. With the *increase in [alcohol] the rate of oxidation increases* in the presence of Ru^{3+} as seen from Table I. The

TABLE I

(A) Effect of [n-Propanol] in the Ce^{4+}-n-propanol reaction

$[Ce^{4+}] = 7{\cdot}20 \times 10^{-3}$ M; $[H_2SO_4] = 0{\cdot}83$ M; $[Ru^{3+}] = 5{\cdot}98 \times 10^{-8}$ M; temp. = 26·4° C

[*n*-propanol] M	0·10	0·15	0·20	0·30	0·40
$v_i \times 10^6$ sec^{-1}	4·53	5·67	6·08	7·01	7·98

(B) Effect of [Iso-propanol] in the Ce^{4+}-Iso-propanol reaction

$[Ce^{4+}] = 7{\cdot}80 \times 10^{-3}$ M; $[H_2SO_4] = 0{\cdot}80$ M; $[Ru^{3+}] = 2{\cdot}98 \times 10^{-8}$ M; temp. = 30·5° C

[iso-propanol] M	0·25	0·50	0·75	1·00	1·50
$v_i \times 10^6$ M sec^{-1}	4·57	9·51	11·00	15·40	15·80

(C) Effect of [Ethyleneglycol] in the Ce^{4+}-ethyleneglycol reaction

$[Ce^{4+}]$ 6·16 × 10^{-3} M; $[H_2SO_4]$ 0·84 M; $[Ru^{3+}] = 1{\cdot}196 \times 10^{-7}$ M; temp. = 35·5° C

[ethyleneglycol] M	0·02	0·05	0·10	0·12	0·15
$v_i \times 10^7$ M sec^{-1}	4·46	7·09	10·06	14·10	22·46

(D) Effect of [Mannitol] in the Ce^{4+}-mannitol reaction

$[Ce^{4+}]$ 7·56 × 10^{-3} M; $[H_2SO_4]$ 1·18 M; $[Ru^{3+}]$ = 1·20 × 10^{-8} M; temp. = 30 C

[mannitol] M	0·05	0·10	0·15	0·20	0·25
v_i 10^6 M sec^{-1}	4·71	6·30	7·23	7·96	8·56