EFFECT OF ANIONS IN Cu(II)-DIAMINE COMPLEXES ON CATALYTIC HYDROLYSIS OF DFP

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MANY examples of metal chelate catalysed hydrolysis of phosphoro and phosphonofluoridates have been reported[1-4]. The Cu(II)-diamine complexes (1:1) are effective catalysts; however, studies have been confined mostly to Cu(II) nitrate complexes. Therefore, in our kinetic studies, attention has been focussed on the effect of anions in CuX_2-diamine (1:1) and (1:2) complexes on the hydrolysis of DFP.

The $CuX_2:L$ complexes (where $X = NO_3^-$, ClO_4^-, CF_3COO^-, CCl_3COO^-) were prepared from mixtures of Cu(II) salts and diamine [L = N, N, N', N'-tetramethylethylenediamine (TMEN)], 1, 3-di-aminopropane (DAP), and N, N, N', N'-tetramethyl-1,2-phenylenediamine (TMPD) either in water or methanol or aqueous methanol.
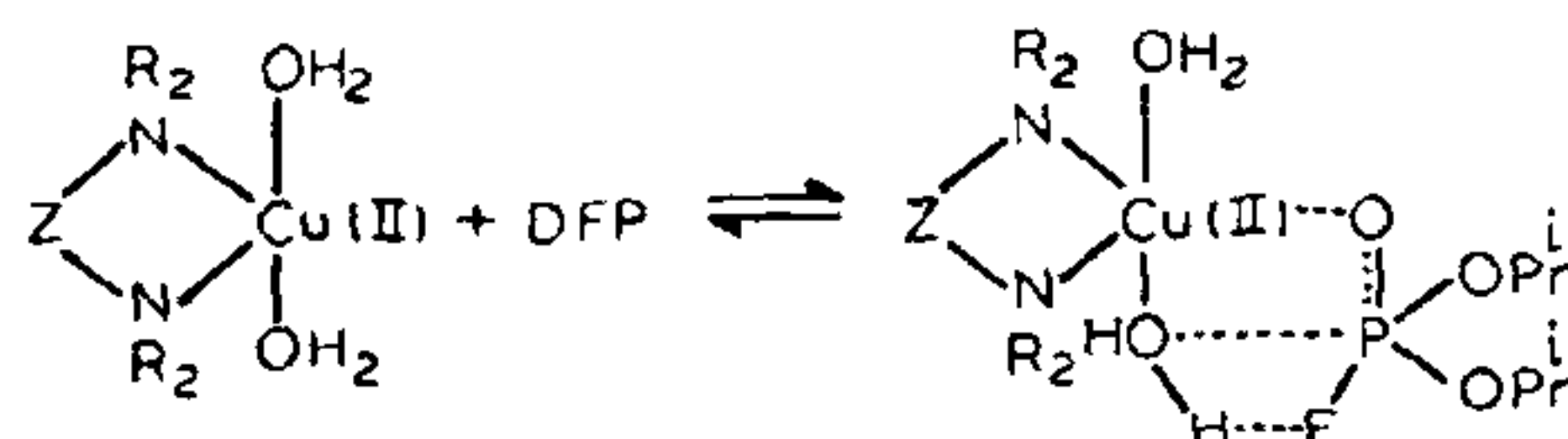
The rate of hydrolysis of DFP was followed by measuring the change in conductivity of liberated HF in unbuffered aqueous solution. Generally the concentrations of metal chelates were kept higher than that of DFP so that the reaction follows first order kinetic rate equation.

A linear plot of $\ln [a/(a-x)]$ against time proved that the reaction follows first order kinetics. The values of experimental $t_{\frac{1}{2}}$ and k_{obs} for various complexes are listed in table 1. Earlier reports showed that only (1:1) complexes are effective

Table 1 *Kinetic results of DFP hydrolysis*

[Conc. of the complex = 5×10^{-3} M, (DEP) = 2.88×10^{-3} M, Temp. 35°C]

Complex	$t_{\frac{1}{2}}$ in s	$k_{obs} \times 10^4 \times s$
Cu(II) perchlorate : TMEN (1:1)	30	231 0
Cu(II) perchlorate : TMPD (1:1)	40	173.3
Cu(II) perchlorate : DAP (1:2)	120	57.8
Cu(II) trichloroacetate : TMEN (1:1)	75	92.4
Cu(II) trichloroacetate : DAP (1:2)	155	44.7
Cu(II) trifluoroacetate : DAP (1:2)	165	42.0
Cu(II) nitrate : TMEN (1:1 mixture)	570	12.16
Cu(II) nitrate : TMEN (1:1)	300	23.1
Cu(II) nitrate : DAP (1:2)	155	44.7
Cu(II) nitrate : TMPD (1:1)	1200	5.8

catalysts and a qualitative suggestion was made regarding the Lewis acid character of the central metal atom in promoting hydrolysis. However, the effect of neither the anions nor the (1:2) metal ligand complexes in the catalytic hydrolysis of fluorophosphates has been reported. During the present study, some of the (1:1) metal complexes could not be isolated and even if isolated with difficulty their stability was low in the reaction medium and consequently showed high apparent $t_{\frac{1}{2}}$ values.

From the table it is evident that the equimolar mixture of Cu(II) nitrate and TMEN gave $t_{\frac{1}{2}} = 570$ s and the isolated Cu(II) nitrate : TMEN (1:1) complex gave $t_{\frac{1}{2}} = 300$ s. This proves that the assumption made earlier[3] that 100% (1:1) complex formation had taken place is not valid and the reason for high $t_{\frac{1}{2}}$ (15 min) obtained by them was because of the TMEN : Cu(II) mixture used. Complexes of Cu(II) : DAP (1:1) could not be isolated and they disproportionate to give (1:2) complex and $Cu(OH)_2$. However, highly stable Cu(II) : DAP (1:2) complexes gave quite high activity. This study shows that both (1:1) and (1:2) complexes are very effective catalysts and the catalytic activity increases with increase of the Lewis acid character of the central metal atom. It is also evident from the table that the bulk of both the anion and the diamine ligand plays an important role in the catalytic activity.

The reaction mechanism proposed by Courtney et al[3] may be operating in our system. But the UV visible monitoring of the reaction system in excess DFP indicates that as hydrolysis proceeds the absorption peak due to complex progressively vanishes with shifting towards the longer wavelength and ultimately appearing at a particular wavelength where the corresponding Cu(II) salt absorbs. This may be due to the neutralization of amine ligand by liberated HF or it could be due to the decomposition of the complex during catalysis, leaving Cu(II) salt and diamine. So the alternative mechanism could be as follows:

TMEN : $Z = (CH_2)_2$, $R = CH_3$
DAP : $Z = (CH_2)_3$, $R = H$
TMPD : $Z = O-C_6H_4$, $R = CH_3$

$$\xrightarrow{\text{Rearranges}} \text{Cu(II) salt. x } H_2O + \text{diaminehydro-}$$
flouride + diisopropylphosphoric acid.

It may be concluded that anion plays a vital role in Cu(II) chelate-catalysed hydrolysis thereby changing the Lewis acid character of the central metal atom. The bulk of the diamine also governs the catalytic activity. The Cu(II) perchlorate complexes of TMEN and TMPD are the most effective catalysts studied so far.

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MID-HOLOCENE SEDIMENTS OF WARNA BASIN, SANGLI DISTRICT, MAHARASHTRA (INDIA)

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ALTHOUGH a few riverine alluvial deposits of the Krishna basin of western upland of Maharashtra State have been dated, data on the age of alluvial deposits along the major tributaries of the Krishna river are lacking due to non-availability of detable material. Recording the occurrence of the carbonized fossil wood from alluvial deposits of Warna river for the first time seems to be significant from palaeogeomorphic and archaeological point of view.

The geology of the Warna basin in the area around Chandoli is marked by a series of Creteceous-Eocene flows of Deccan Trap flood basalts. They are capped by laterite duricrust at higher level and by the riverine deposits in the valley sections. Along either banks of Warna river near Chandoli (73°52'5"—17°8'55"), the basal semiconsolidated conglomeratic bed is overlain by fine red lateritic soil. The contact of these two horizons is marked by (about 0.30 m thick) blackish red soil containing organic matter in which fossil wood has been encountered during the foundation excavation of the Warna dam (figure 1). The lower portion of the red fine lateritic soil is devoid of gravels, pebbles, cobbles, etc. while the upper portion of
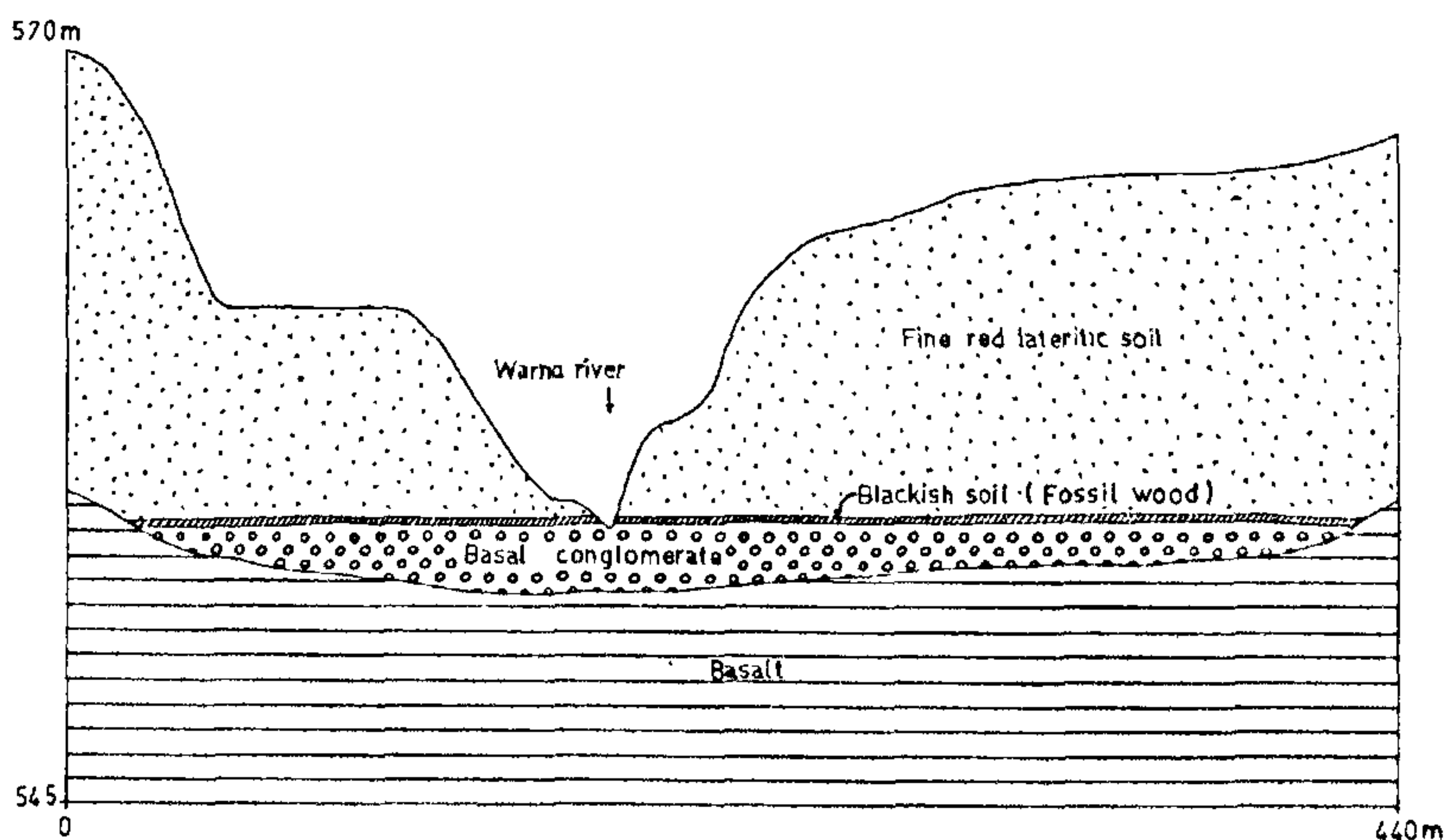

Figure 1. Geological section across Warna valley at Chandoli.