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Hydrolysis of diisopropyl phosphorofluoridate catalysed by copper (II)-diamine complexes

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The hydrolysis of diisopropylphosphorofluoridate (DFP) has been studied using various diamine complexes of Cu salts. The complexes of Cu(II) perchlorate salt have been found to be the most effective catalysts. Lewis acid character of the central Cu metal atom is enhanced by strong anion which in turn increases the catalytic activity.

Most of the phosphono and phosphoro esters which are very useful insecticides are highly toxic and are also reported as chemical warfare agents. Rapid hydrolysis of such compounds is considered as one of the methods for their effective detoxification. Wagner-Jauregg *et al.*[1] studied Cu(II)-bipyridyl sulphate catalysed hydrolysis of diisopropylphosphorofluoridate (DFP) under unbuffered condition at a constant *p*H. Augustinsson and Heimbürger[2] described the effectiveness of Cu(II), Ni(II), Ag(I), Au(III), and Pd(II) salts in accelerating the hydrolysis of N,N-dimethylethylphosphorocyanidate (Tabun). Copper (II) nitrate complex of N,N,N′,N′-tetramethylethylenediamine (TMEN) (1:1 mixture) was reported[3], to bring down the half-lives of DFP and isopropylmethyl phosphonofluoridate (Sarin) to 15 min and 1.5 min respectively at *p*H 7.

Menger *et al.*[4] studied the hydrolysis of *p*-nitrophenyldiphenylphosphate (PNPDPP) and pinacolylmethylphosphonofluoridate (Soman) catalysed by micellar Cu(II) diamine complex. They found the k_{obs} for the hydrolysis of PNPDPP very high and the half-life of Soman at *p*H 7.0 was 0.85 min. But work so far done in this area suffers from certain disadvantages i.e. in some cases the hydrolysis takes longer time while in others the solubility of the catalyst in water is low or the catalysts are found effective at high *p*H only.

Both Courtney *et al.* and Menger *et al* have confined their work to complexes of Cu(II) nitrate with different diamines or of Cu(II) chloride with diamines having long alkyl chain. Considering the two influencing factors, viz. solubility of the complexes and electrophilicity of the central metal atom, presently we have investigated the hydrolysis of DFP using diamine complexes of Cu(II) salts with different anions. Diamines of varied chain lengths were also studied.

Materials and Methods

The complexes $CuX_2{:}L_2$ (where $X = NO_3^-$, ClO_4^-, CCl_3COO^- and CH_3COO^-, L = diamine) were prepared by mixing 1:2 molar quantities of Cu (II) salt and diamine [N,N,N′,N′-tetramethylethylenediamine (TMEN), 1,3-propanediamine (DAP) and N,N,N′,N′-tetramethyl-1,2-phenylenediamine (TMPD)] in 70% aqueous ethanol, recrystallised from aq. ethanol and characterised by elemental analyses. Stability of the complexes was studied spectrophotometrically by monitoring the UV/visible absorption peak of the aqueous solution of the complexes at 35°C. The conductivity measurements were carried out using digital conductivity meter Apx-185 and the cell was kept in a Julabo F-50 Ultratemp 2000 thermostat.

Diisopropylphosphorofluoridate (DFP) was synthesised by the reported procedure and its purity was checked by GLC. The hydrolysis of DFP was followed by measuring the change in conductivity of liberated HF in unbuffered aqueous solution. Generally ionic strength was not maintained and the reaction kinetics were followed under pseudo-first order condition viz. [metal chelate] > > [DFP]. Linear first order plots were always obtained for atleast upto three half-lives. The rate constants were calculated from the linear plot of ln $(a/(a-x)$ versus time. Kinetic runs carried out always in duplicate gave rate constants with an uncertainity of less than ± 5%.

Results and Discussion

From Table 1 it is seen that k_{obs} values did not

Table 1 – Pseudo-first order rate constants for the metal-chelate catalysed hydrolysis of DFP

Complex	10^3[complex] mol dm^{-3}	10^3[DFP] mol dm^{-3}	Temp. °C	10^3 k_{obs} (s^{-1})	Half life $t_{1/2}$(s)	*Ea* (kcal/mol)
Cu(II) perchlorate:TMEN (1:2)	7.5	2.88	35	34.0	20.4	3.0
	5.0	2.88	35	18.0	38.5	
	5.0	1.44	35	17.5	39.6	
	5.0	0.72	35	17.8	38.9	
	5.0	2.88	27	16.0	43.3	
	5.0	2.88	17	13.0	53.3	
Cu(II) trichloroacetate:TMEN (1:2)	5.0	2.88	43	17.0	40.8	9.0
	5.0	2.88	35	12.0	57.8	
	5.0	2.88	27	8.0	86.6	
Cu(II) nitrate:TMEN (1:1)	5.0	2.88	35	3.5	198.0	9.0
	5.0	2.88	27	2.4	288.8	
Cu(II) nitrate:TMEN (1:2)	5.0	2.88	42	14.45	48.0	9.2
	5.0	2.88	35	10.0	69.3	
	5.0	2.88	27	6.67	103.9	
Cu(II) formate:TMEN (1:2)	5.76	2.88	35	0.75	924.0	–
Cu(II) acetate:TMEN (1:2)	5.76	2.88	35	0.55	1260.0	–
Cu(II) perchlorate:TMPD (1:2)	5.0	2.88	35	19.0	36.5	3.33
	5.0	2.88	27	15.5	44.7	
	5.0	2.88	17	12.0	57.8	
Cu(II) perchlorate:DAP (1:2)	5.0	2.88	35	6.0	115.5	9.33
	5.0	2.88	27	4.0	173.3	
	5.0	2.88	17	2.4	288.8	
Cu(II) trichloroacetate:DAP (1:2)	5.0	2.88	35	5.0	138.6	8.0
	5.0	2.88	27	3.0	231.0	
Cu(II) nitrate:DAP (1:2)	5.0	2.88	35	8.0	86.6	8.2
	5.0	2.88	27	5.0	138.6	

change with [DFP] (0.72×10^{-3} mol dm^{-3} to 2.88×10^{-3} mol dm^{-3} at 5×10^{-3} mol dm^{-3} of Cu(II) perchlorates: TMEN complex). This also shows that the reaction is first order in [substrate]. The activation energy values are also given in Table 1. Half life ($t_{1/2}$) of each reaction was calculated from the equation $t_{1/2} = 1/k (\ln a/(a-x))$.

In phosphate buffer (*p*H 6 and 7) and borax-boric acid buffer (*p*H 8) the complexes are unstable whereas in the TRIS buffer the complexes are very stable but the catalytic activity decreases atleast 10-15 times. Possibly the amino groups of TRIS molecules occupy the active sites of the metal ion which would normally be accessible to the P=O functionality of DFP during the catalytic process[5].

Effect of ionic strength was studied using different [KCl] and was found to be negligible on the rate of reaction. From Table 1 it is observed that the rate of hydrolysis is minimum in the case of Cu(II) acetate-TMEN complex and maximum for Cu(II) perchlorate-TMEN. As we proceed from complex of weak acid salts of copper to those of strong acid salts, the rate of hydrolysis increases many-fold and is 6700 times faster than that in absence of any catalyst. In the complexes showing a faster rate of hydrolysis, the Lewis acid character of the central metal atom is also found to increase. This is evident from the Bronsted type plot (Fig. 1) which shows a linear relationship between *p*Ka of various acids and log of k_{obs} values of TMEN complexes of Cu(II) salts of the corresponding acids at 35°C.

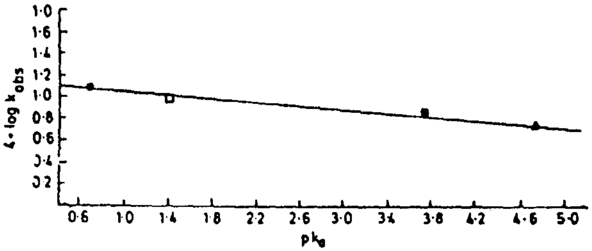


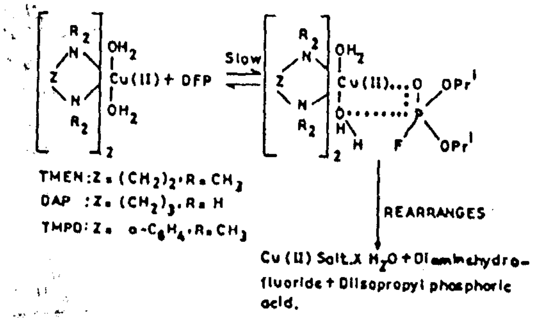
Fig. 1 – Bronsted type plot of log k_{obs} versus pk_a (●-trichloroacetic acid; □-nitric acid; ⏀-formic acid; △-acetic acid)

Earlier reports[3] showed that only 1:1 complexes acted as effective catalysts. It has now been observed that 1:1 complexes are not only very difficult to isolate but also if at all they are isolated, their stability is low in the reaction medium resulting in high apparent $t_{1/2}$ values. It is clear from Table 1 that in the presence of Cu(II) nitrate-TMEN (1:1) complex k_{obs} is low relative to that in presence of Cu(II) nitrate-TMEN (1:2). Further Copper (II) nitrate-TMEN 1:1 complex becomes turbid in aqueous solution. This could be due to disproportionation reaction in solution to form more stable (1:2) complex, which is further supported by the same values of activation energies in the reaction catalysed by 1:1 and 1:2 complexes. The low k_{obs} values in the case of 1:1 complex could be due to the low effective concentration of 1:2 complex after disproportionation. Presently it has been observed that the aqueous solutions of 1:2 complexes are very stable at 35°C and λ_{max} values do not change appreciably even upto 5 days with the exception of Cu(II) perchlorate-TMPD complex which decomposed after 24 hrs.

The activation energies were calculated and found to be very low specially in the case of reactions catalysed by Cu(II) perchlorates-TMEN and Cu(II) perchlorate-TMPD complexes.

The chain length and substitution on nitrogen of the diamines by methyl groups helped to enhance the catalytic activity of the complexes (Table 1). Complexes of N,N,N',N'-tetramethyl-1,3-propanediamine, 1,4-butanediamine and 1,2-phenylenediamine could not be prepared. In the case of TMPD only two complexes could be prepared. It is difficult to derive a correlation between the chain length and catalytic activity. The k_{obs} values of TMEN and TMPD complexes are almost the same; while ethylenediamine or 1,2-phenylenediamine complexes showed hardly any catalytic reactivity, N,N,N',N'-tetramethyl substituted diamine complexes are very reactive and even DAP complexes are quite reactive; thus substitution could play a major role in promoting the catalytic activity by increasing the basicity required to form a better complex with the copper salt.

The reaction mechanism proposed by Courtney *et al.*[3] or Menger *et al.*[4] may be operating in the present system also. Menger *et al* showed that their complexes had got catalytic turnover while Courtney *et al.* mentioned nothing about the fate of the complexes. UV/visible monitoring of the reaction of Cu(II) trichloroacetate-TMEN complex with excess DFP indicates that as hydrolysis proceeds the absorption peak at 570 nm due to the complex progressively disappears and a new peak at 680 nm makes its appearance. The 680 nm peak is due to Cu(II) trichloroacetate. Similar effect was seen by incremental addition of HF solution to a solution of Cu(II) trichloroacetate-TMEN complex. This may be due to the neutralisation of amine ligand by liberated HF but the possibility of decomposition of the complex during catalytic process, giving Cu(II) salt and diamine cannot be excluded. In any case the reaction seems to proceed stoichiometrically without giving any turnover of the catalyst. The very high catalytic activity of tetramethyl substituted ethylenediamine and N,N,N',N'-tetramethyl-1,2-phenylenediamine complexes indicate that the substitution on the nitrogen atom may help the diamine ligand to come out from the "transition complex" formed between the Cu(II) diamine complex and DFP during hydrolysis. Though the complex formation between the Cu(II) diamine complex and DFP is not evidenced by spectral data, our study on parathion showed that blue Cu(II) diamine complex forms a green complex with parathion and the 570 nm peak shifted atleast by 70 nm towards longer wavelength with simultaneous hydrolysis of parathion; so it would not be unreasonable to think that complex formation occurs prior to hydrolysis of DFP. From these results, the mechanism of Cu(II) diamine complex catalysed hydrolysis can be proposed as given in Scheme 1.



SCHEME 1

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