TABLE.I—*Contd.*

Complex	%Co		%N	Band I cm^{-1}	Band II cm^{-1}
Co (salpn) (tropolone)	Found:	12·3	5·7	16000 (2·54)	25640 (4·09)
	Reqd.:	12·83	6·09		
Co (salpn) (acan)	Found:	11·1	8·4	16950 (2·50)	25510 (3·78)
	Reqd.:	11·46	8·16		
Co (salpn) (oxine)	Found:	12·0	9·0	17120 (2·60)	25250 (3·94)
	Reqd.:	12·22	8·70		

a Figures in the parentheses indicate log ∊.

b Abbreviations: acac = deprotonated anion of acetylacetone; acan = deprotonated anion of acetoacetanilide; oxine = deprotonated anion of 8-hydroxyquinoline.

$^1A_{1g} \rightarrow {}^1T_{2g}$ transition. The *cis* spanning of the bidentate ligand in the complexes force the quadridentate ligands saltn and salpn to coordinate to cobalt (III) in a nonplanar twisted configuration similar to salen in Co (salen) (β-diketone)[3].

The synthesis of mixed ligand complexes utilising other bidentate NO, NN and OO donor ligands and also the synthesis of Co(acen) (BB) (where acen H$_2$ = N, N'-ethylenediaminebis (acetylacetoneimine) and BB = bidentate ligand) are in progress.

The details of the work will be reported later.

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KINETICS OF REACTIONS OF TERTIARY AMINES WITH BENZYL HALIDES

BROWN and Eldred[1] and Brown and Fried[2] have investigated quaternisation of a number of tertiary amines with alkyl halides. Baker and Nathan[3] have compared the reactions of pyridine and α-picoline with arylbromide and alkylbromides and the differences in reactivities have been attributed to differences in energy of activation. Solvent influences on certain quaternisation processes have also been studied by Padmanabhan and Anantakrishnan[4]. This note deals with the kinetics of reactions of pyridines, quinoline, isoquinoline and their derivatives with benzyl and substituted benzyl chlorides in nitrobenzene and nitrobenzene-ethanol mixture and the kinetic data have been used to compute the nucleophilicity parameters of the bases for the first time.

Kinetics has been followed by Volhard's method using A.R. grade substances mostly, except a few compounds which were purified using standard procedures.

The second order rate constants for the reactions of tertiary bases with benzyl halides have been calculated using the usual rate expression except in a few cases in nitrobenzene medium, where equilibrium was attained and in such cases the rate constant was evaluated using the modified rate expressions[5].

As seen from Table I, plots of log *k* for pyridines VS Pka are fairly linear except with α-picoline. The order of reactivity is γ-picoline > β-picoline > pyridine > α-picoline. Plots of log *k* of bicyclic bases VS Pka shows considerable scatter probably due to want of accurate Pka values in the solvent system studied. Among the bicyclic bases, isoquinoline reacts faster than quinoline but the order is reversed when quinoline nucleus is substituted with a methyl group.

Among the benzyl chlorides, *p*-methyl benzyl chloride reacts fastest due to the electron releasing nature of the methyl substituent. The lower reactivity of chlorobenzyl chlorides can be attributed to the electron attracting nature of the substituents.

The reactions in nitrobenzene alcohol (80 : 20 V/V) are uniformly faster than in nitrobenzene. The higher reactivity in the mixed solvent is due to the protic character of the solvent.

TABLE I

Second order rate constants ($l.$ moles^{-1} min^{-1}) for the reaction of tertiary amines with benzyl halides

Solvent : Nitrobenzene   Temperature 80° C.

Base	Pka*	Benzyl chloride	p-Methyl benzyl chloride	p-Chloro-benzyl chloride	o-Chloro-benzyl chloride
Pyridine	5·17	0·006 (·014)	0·010 (·030)	0·005 (·011)	0·005 (·011)
α-Picoline	5·97	0·001 (·0025)	0·0021 ..	0·00075 (·0025)	0·00083 (·0025)
β-Picoline	5·68	0·0112 (·0235)	0·0132	0·0085 (·018)	0·011 (·0225)
γ-Picoline	6·02	0·0121 (·040)	..	0·0090 (·020)	0·0121 (·023)
Quinoline	4·85	0·00049 (·0016)	0·0018 (·0025)	0·00049 (0·00083)	0·00040 (·0009)
Isoquinoline	5·14	0·0083 (·016)	0·011 (·031)	0·0073 (·014)	0·0079 (·016)
2-Methyl quinoline	5·42	0·0016	0·0029	0·0011	0·0017
3-Methyl isoquinoline	5·64	0·0011	0·0025	0·00067	0·00085

* At 25° C in aqueous medium taken from *Physical Methods in Organic Chemistry*, Vol. I, by Braude and Nachod for purposes of comparison.

Values in parentheses are rate constants in Nitrobenzene-alcohol (80 : 20 V/V) mixture at 80° C.

Application of Tommila equation.—Application of the Tommila equation[6] suggests a positive reaction centre in benzyl chloride as seen from the nature of log Ks/ku values given in Table II.

TABLE II

Ratio of rate constants of substituted and unsubstituted benzyl chlorides in nitrobenzene and nitrobenzene-alcohol

Substrate	X	Base	log Ks/Ku Nitro-benzene	log Ks/Ku Nitro-benzene ethanol (80 : 20 V/V)
X-C₆H₄-CH₂Cl	P–CH₃	Pyridine	+0·22	+0·32
	P–Cl		−0·08	−0·10
	P–CH₃	Quinoline	+0·57	+0·20
	P–Cl		..	−0·28
	O–Cl		−0·10	−0·25

TABLE III

Nucleophilic reactivity constants of tertiary bases

     α (For Benzyl chloride) $= 3·53$,

     β (for Benzyl chloride) $= -0·128$

Substrate : Benzyl chloride   Temperature : 80° C

Solvent : Nitrobenzene

Base	H	Nucleophilicity	E$_n$
Pyridine	6·91	4·80 (4·80)	1·44 (1·44)
α-Picoline	7·71	3·94 (3·90)	1·25 (1·24)
β-Picoline	7·42	5·04 (5·11)	1·51 (1·53)
γ-Picoline	7·76	5·33 (5·16)	1·59 (1·55)
Quinoline	6·59	3·72 (3·55)	1·16 (1·11)
Isoquinoline	6·88	4·88 (4·96)	1·45 (1·47)
2-Methyl quinoline	7·16	3·96	1·24
3-Methyl quinoline	7·38	4·02	1·26

Values in parentheses are in nitrobenzene-alcohol (80 : 20 V/V).

Application of linear free energy relationship.— Swain-Scott[7] and Edwards[8] equations have been applied to the kinetic data and parameters like nucleophilicity and E_n values for the bases used have been computed in nitrobenzene and nitrobenzene-alcohol mixtures which help in understanding the mechanism of the process to some extent[9]. The parameters are given in Table III.

The parameters are identical in nitrobenzene and nitrobenzene-alcohol mixture demonstrating the operation of identical mechanism in both the solvent systems.

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PHYSICO-CHEMICAL STUDIES OF SOME BIVALENT METAL ION CHELATES OF N-ACETYLACETONE ORTHANILIC ACID

THE results of physico-chemical studies on the chelates of N-Acetylacetone orthanilic acid (H_2AO) with some bivalent metal ions are reported in this note.

Orthanilic acid supplied by SCHUCHAROT MUNCHEN was used. All other compounds were of BDH grade. The molecular weights, elemental analysis, magnetic susceptibility and electronic absorption spectra were determined by standard methods as reported earlier[1].

Preparation of H_2AO and its metal chelates.— H_2AO Schiff base was prepared by the method of Pfeiffer *et al.*[2]. The metal chelates were synthesised by the method of Yamada *et al.*[3][4] and their pyridine solvates by the method reported earlier[1].

Analysis : Found C, 51·81 ; H, 4·99 ; N, 5·47 ; S, 12·41. Calcd. for $C_{11}H_{13}NSO_4$. C, 51·96 ; H, 5·11 ; N, 5·51 ; S, 12·59%, m.p. 160°.

Results and Discussions.—Elemental analysis, molecular weight and magnetic data of the hydrated chelates are given in Table I.

The molecular weight data indicate that Fe (II). Co (II). Ni (II) and Cu (II) chelates possess the composition [MLX_3] where M represents the metal ion, $X = H_2O$ or Py and $LH_2 = [C_{11}H_{13}NSO_4]$. The magnetic moment values reveal the presence of 4, 3, 2 and 1 unpaired electrons in the Fe (II), Co (II), Ni (II) and Cu (II) chelates respectively. The high magnetic moment of Co (II) chelate appears to be due to spin-orbit coupling.

The electronic absorption spectra of these chelates were studied both in dioxane and pyridine solu-

TABLE I

Elemental analyses, molecular weights and magnetic moments of the metal chelates of N-acetylacetone-orthanilic acid

Metal chelate	Mol. wt.	Metal %	N %	H_2O %	μ_{eff} (B.M.) at 298° K
[Fe($C_{11}H_{11}NSO_4$) X_3]	357 (362)	14·32 (15·46)	3·81 (3·86)	14·87 (14·91)	5·48
[Co($C_{11}H_{11}NSO_4$) X_3]	369 (365)	16·01 (16·16)	3·80 (3·83)	14·71 (14·79)	5·12
[Ni($C_{11}H_{11}NSO_4$) X_3]	365 (364·7)	16·80 (16·92)	4·07 (4·11)	14·76 (14·80)	3·11
[Cu($C_{11}H_{11}NSO_4$) X_3]	360 (369·5)	17·00 (17·18)	3·69 (3·78)	14·51 (14·61)	1·89
[Pd($C_{11}H_{11}NSO_4$) X]	370 (376)	28·07 (28·19)	3·61 (3·72)	4·71 (4·79)	..
[Zn($C_{11}H_{11}NSO_4$) X]	339 (335·4)	19·31 (19·49)	4·10 (4·17)	5·30 (5·36)	..
[Cd($C_{11}H_{11}NSO_4$) X]	377 (382·4)	29·27 (29·39)	3·59 (3·66)	4·59 (4·70)	..
[UO_2($C_{11}H_{11}NSO_4$) X]	545 (540)	49·90 (50·00)	2·54 (2·59)	3·31 (3·33)	..

Calculated values are given in parentheses. X refers to H_2O. Zn (II), Pd (II), Cd (II), UO_2 (II) chelates were found to be diamagnetic, as expected.