

rate. This has also been observed by Mushran and co-workers<sup>4</sup>.

In view of the fact that several species of CAT (depending on pH) are current in literature, a systematic pH profile was attempted for the DMSO-CAT reaction. The reaction exhibits a rate maximum at pH 4.5. Second order rate constants at pH 4.5, 5.4 and 6.8 are 164.0, 59.0 and 1.4 respectively at 35°C. Such pH dependence has been observed earlier in the oxidation of alcohols and chlorination of amines by CAT, and is attributed to HOCl being the active species, whereas below this pH, RNHCl is postulated to be the active species which might have been responsible for the insensitivity to HClO<sub>4</sub> in the range 0.01 to 0.1 M. We rule out the mediation of dichloramine-T, because no second order dependence on [CAT] is observed under these conditions. The reactions are greatly accelerated in aqueous HOAc/NaOAc buffer (10% aqueous HOAc, NaOAc = 0.02 M  $k_2 = 16.2 \text{ l.m}^{-1} \text{ min}^{-1}$  at 35°C). Such specific acetate ion catalysis has been observed earlier in DMSO-Br<sub>2</sub> oxidation<sup>3</sup>. The reactions are retarded in aqueous HOAc and aqueous ethanol at constant acidity, quite in consonance with the dipole-dipole nature of these reactions (Table II).

The reactions are sluggish from pH 6-8 and no perceptible oxidation occurs under alkaline conditions. To sum up it can be said that though the reaction has no dependence on [HClO<sub>4</sub>] in the range of this study, it is not independent of [H<sup>+</sup>] in the wider sense and the nature of the CAT species should be taken into account.

TABLE II

Solvent effect: Temp.: 35°C  
DMSO = 0.0043 M, HClO<sub>4</sub> = 0.05 M,  
NaClO<sub>4</sub> = 0.025 M, CAT = 5.0 × 10<sup>-4</sup> M

Solvent	$k_2 \text{ l.m}^{-1} \text{ min}^{-1}$	Solvent	$k_2 \text{ l.m}^{-1} \text{ min}^{-1}$
10% HOAc	6.4	10% EtOH	5.2
20% HOAc	4.3	20% EtOH	3.7
30% HOAc	3.0	30% EtOH	2.5

It is already mentioned that the reaction of DMSO-CAT in alkaline medium is sluggish and this has been catalysed by OsO<sub>4</sub>. The following kinetic features are observed:

(i) Zero order in [DMSO] and [OH<sup>-</sup>]. In the [DMSO] range 35.0 × 10<sup>-2</sup> to 0.44 × 10<sup>-2</sup> M,  $k_1$  is essentially constant (6.8 × 10<sup>-3</sup> min<sup>-1</sup>). In the [OH<sup>-</sup>] range 0.1 to 0.4 M NaOH,  $k_1 = 3.0 \times 10^{-3} \text{ min}^{-1}$  at 60°C.

(ii) First order in [CAT] and [OsO<sub>4</sub>]

The dependence on [OH<sup>-</sup>] in the oxidation of HCHO and CH<sub>3</sub>CHO, is obvious from a consideration of the

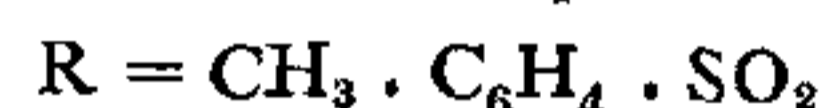
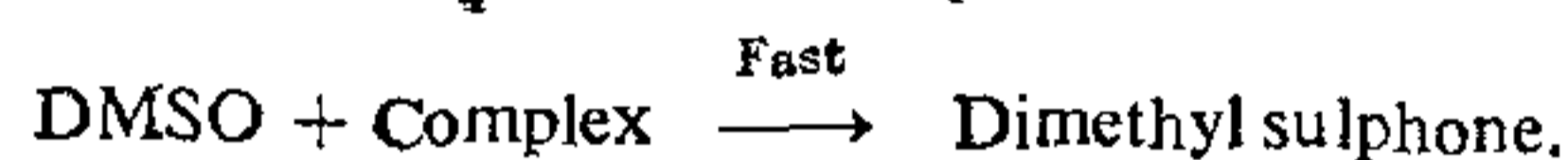
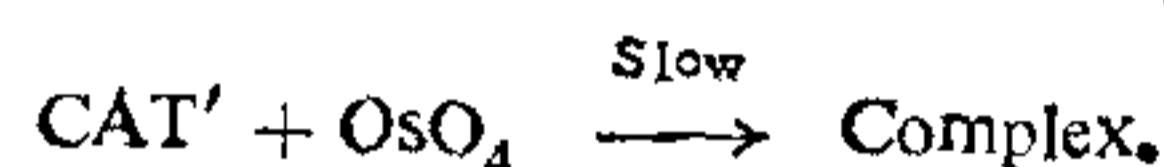
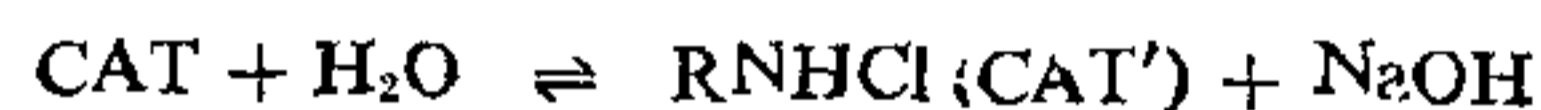
formation of aldehyde hydrate which loses a H<sup>-</sup>. Such a possibility is not there in these reactions and these are independent of OH<sup>-</sup> in the range studied.

TABLE III

NaOH = 0.1 M, CAT = 5.0 × 10<sup>-4</sup> M, Temp.: 60°C  
DMSO = 35 × 10<sup>-2</sup> M

[OsO <sub>4</sub> ] 10 <sup>6</sup> M	10 <sup>3</sup> $k_1 \text{ min}^{-1}$
3.9	1.6
7.8	2.8
11.7	3.7
15.6	5.8
19.5	6.8

Addition of *p*-toluene sulphonamide (0.0005 M) causes retardation which points to a specific negative salt effect. The following scheme is consistent with our kinetic data:



That, these reactions are dependent on a complex between CAT and OsO<sub>4</sub> is well proven by earlier workers with other substrates<sup>4</sup>. The stoichiometry is 1:1 and the product is dimethyl sulphone.

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#### MICRO ANALYSIS OF Ni(II), Co(II), Pd(II) AND Ti(IV), Y(III), Zr(IV) BY COMBINED THIN-LAYER CHROMATOGRAPHY AND RING COLORIMETRY

THE combination of thin-layer chromatography (TLC) and Weisz Ring Oven has been shown to be successful by Johri *et al.*<sup>1-5</sup> for the micro analysis of metal ions. The present paper relates to the use of some new chromogenic reagents like

diphenyl thiovioluric acid<sup>6</sup> (DPHTVA) tropolone and quercetin in the micro analysis of Ni(II), Co(II), Pd(II) and Ti(IV), Y(III), Zr(IV). Also, the use of fluorescent support on thin-layers has been avoided which creates difficulties with certain solvent systems.

*Experimental*

Analytical grade salts were dissolved in double distilled water to give 1 mg/ml of stock solutions.

*Visualising Agents.*—M/100 diphenyl thiovioluric acid (DPHTVA) in acetone, M/100 quercetin (Fluka) in alcohol, M/50 tropolone (Aldrich) and 0.1% solution of alizarin in alcohol were employed.

*Separation of Ni(II), Co(II) and Pd(II)*

1–3  $\mu$ l of each of the test solutions was applied separately at three points on silica gel 'G' coated glass plate along the base line, from one end as a reference with help of Hamilton syringe. The mixture of the three ions was applied at the fourth point. The plate was developed by the ascending technique in MIBK–HCl (25 : 4 ; v/v) solvent system for 35 minutes so as to achieve clean separation of the ions. The plate was removed from the jar, thoroughly dried in a stream of hot air and the separated metal ions were located with sprays of diphenyl thiovioluric acid followed by 0.1% aq. NaOH.

*Separation of Ti(IV), Y(III) and Zr(IV)*

This separation was carried out on cellulose support using the solvent system, acetone-1 N HCl (25 : 2 ; v/v). The plate was developed for 15 minutes. The remaining procedure is the same as given in the previous separation.

Results are given in Table I.

*Ring Colorimetric Determination of the Chromatographed Constituents*

For the determination of the metal ions, one drop of the known mixture of Ni(II), Co(II) and Pd(II) at one end and a drop of the unknown test sample at the adjacent end of the thin-layer plate were applied. The plate was developed as described earlier. Half portion of the plate, containing the known separated constituents, was subjected to sprays of chromogenic reagent (Table I) leaving the other half unaffected. Next, the respective spot region of the particular metal ion on the thin layer (unsprayed) as judged by comparing it with the visualized portion of the plate was sucked out by means of a micro vacuum collector. The individual metal ions from the sucked out material were eluted with water on a Whatman No. 41 filter paper of 55 mm diameter, placed on the ring oven, maintained at 110° followed by its washings into the ring zone. The same procedure was repeated for the other metal ions. The individual metal ions were then treated with the reagents listed in Table II.

For the evaluation, the intensities of the coloured rings obtained with the different cationic species were compared visually with those of standard rings prepared separately<sup>7</sup> and corresponding to 1–10  $\mu$ l of standard solution. Results of a few representative determinations are given in Table II.

Similar determination procedure was adopted for Ti(IV) Y(III) and Zr(IV).

In the case of Ni(II), Ti(IV) and Y(III), because of the yellow colour of the developed rings, the efficient visual comparison for their evaluation was not possible. This difficulty, however,

TABLE I  
*Detection of ions after TLC separation*

Metal ion	Spray reagent	Colour	R <sub>f</sub>	Limit of Identification $\mu$ g
Ni(II)	DPHTVA	Yellow	0.82	0.30
Co(II)	DPHTVA	Reddish-brown	0.64	0.09
Pd(II)	DPHTVA	Dark-brown	0.28	0.15
Ti(IV)	Quercetin	Brownish-red	0.62	0.20
Y(III)	Quercetin	Yellow	0.34	0.16
Zr(IV)	Quercetin	Yellow	zero	0.30



TABLE II  
Representative results of determination

Ion determined	Developing agent	Colour of the ring	Ion taken mg/ml	Ion found mg/ml	Error %
Ni(II)	DPHTVA	Yellow	0.80	0.82	+2.5
			1.20	1.14	-5.0
			1.60	1.55	-3.1
Co(II)	DPHTVA	Reddish-brown	0.60	0.58	-3.3
			0.90	0.92	+2.2
			1.20	1.15	-4.1
Pd(II)	DPHTVA	Brown	0.75	0.75	0.0
			1.00	1.05	+5.0
			1.50	1.42	-5.3
Y(III)	Quercetin	Yellow	0.84	0.82	-2.4
			0.42	0.40	-4.7
			1.26	1.18	-6.3
Ti(IV)	Tropolone and 6 M HCl	Yellow	0.95	0.92	-3.1
			0.60	0.58	-3.3
			0.90	0.85	-5.5
Zr(IV)	1M HCl and alizarin i	Reddish-violet	0.75	0.72	-4.0
			1.00	0.94	-6.0
			1.50	1.60	+6.6

was over come by viewing the rings through blue glass both for standard scale as well as for test samples.

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#### DETERMINATION OF 3-AMINOPYRIDINE IN ETHYL METHYL KETONE MEDIUM

PETERSON *et al.*<sup>1</sup> carried out the potentiometric titrations of heterocyclic nitrogen bases such as pyridine with stannic chloride and other non-protonic acids in selenium oxychloride medium. They employed the technique of Muller "retarded" electrode system in the titrations. Garber *et al.*<sup>2</sup> effected the visual titrations of pyridine with stannic chloride in thionyl

chloride medium using crystal violet and malachite green in solid form. In the present work an attempt has been made to titrate pyridine bases against stannic chloride in ethyl methyl ketone medium. The end points were located with the aid of visual and potentiometric techniques.

Ethyl methyl ketone (B.D.H.) was dried over anhydrous potassium carbonate for 24 hours and then fractionally distilled. 3-Aminopyridine (Koch-light) and stannic chloride were used without purification. Solutions of 3-aminopyridine and stannic chloride were prepared in ethyl methyl ketone. The amine solution containing 2 to 3 drops of methyl orange indicator (0.1% solution in ethyl methyl ketone) was titrated with stannic chloride. The colour changed from yellow to pink at the end point.

Potentiometric titrations were performed with Elico pH meter employing glass electrode. Characteristic 'S'-shaped curves were obtained by plotting EMF against the volume of stannic chloride added. The exact end point was located by the calculation method<sup>3</sup>. The results of visual and potentiometric titrations are presented in Table I.

The results (Table I) show that 3-aminopyridine can be determined with an error of less than 1% by visual titrations employing methyl orange as indicator. The determination of base can be effected potentiometrically also with an error, less than 1%.