

fastest at pH 4.7 at which pH value the rate of formation and equilibrium concentration of dichloramine-T in chloramine-T solutions are known to reach the maximum.<sup>5</sup>

Protonation of the sulphoxides appears to be essential for their oxidation by chloramine-T solutions. In alkaline media, no oxidation occurs. Reaction between diphenyl sulphoxide and RNHCl or RNCl<sub>2</sub> in organic phase such as carbon tetrachloride and benzene was found to be very limited.

The kinetics of oxidation of various sulphoxides with chloramine-T in acid media both in presence and absence of chloride ions are being worked out in order to elucidate the mechanism of the reactions.

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### SPECTROPHOTOMETRIC INVESTIGATIONS OF TITANIUM (IV)-OXINE N-OXIDE COMPLEX

THOUGH polyphenols, *o*-hydroxy phenyl carboxylic acids and hydroxy- $\gamma$ -pyrones have been suggested as sensitive colorimetric reagents for titanium (IV), the use of these ligands is limited due to easy auto-oxidation of these compounds,<sup>1</sup> especially in alkaline medium. Hence there is need for more satisfactory reagents.

Oxine N-oxide resembles the peri-dihydroxy compounds in forming a six-membered chelate ring through two oxygen donors. It has been observed that on the addition of aqueous oxine N-oxide to aqueous titanium (IV) chloride, an orange-yellow water-soluble complex is produced and the present communication deals with its spectrophotometric investigations.

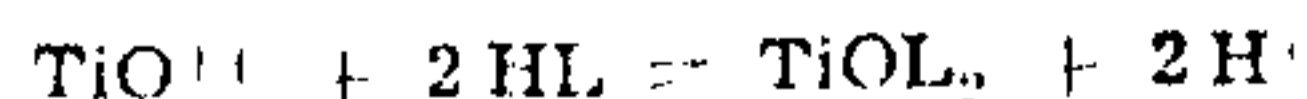
The absorption spectrum of the solution containing  $8 \times 10^{-5}$  M titanium (IV) and varying concentration of the reagent (metal: reagent ratio varying from 1:1 to 1:10) at pH 2.5 against reagent as blank showed the

presence of a single absorption maximum at 405 m $\mu$ , thereby indicating the presence of a single complex. The absorbance of the solution containing titanium (IV) and oxine N-oxide in the molar ratio 1:10 remained constant and maximum at pH 4.2-5.0. At higher pH, the solutions became opalescent due to the hydrolysis of titanium (IV), while at lower pH the complex formation is incomplete. For complete colour development at pH 4.2-5.0, a minimum of 350 times reagent concentration is necessary. Beer's law is not obeyed in case of aqueous solution of this complex because of its high dissociation and the low solubility of the reagent in water. The molar absorption of the complex with 400 times reagent concentration, using reagent as blank at 405 m $\mu$  was found to be  $1.0 \times 10^4$  per mole of titanium (IV). But the reagent has higher solubility in ethanol and 50% aqueous ethanol was used as a medium for the spectrophotometric determination of titanium (IV), and it was observed that under these conditions, a minimum of 300 times reagent concentration was necessary; and the complex obeyed Lambert-Beer's law within 0.2 to 2.0 ppm titanium (IV) in presence of sufficient reagent.

During the estimation of 0.5 ppm Ti(IV), the limit of tolerance of foreign ions was found to be 8 ppm for thorium (IV), 4 ppm for cobalt (II), 4 ppm for nickel (II), 15 ppm for acetate, 4 ppm for tartrate and 1 ppm for citrate ions. Iron (III), chromium (III), vanadium (IV), zirconium (IV), cerium (IV), uranium (VI), sulphate, oxalate and phosphate ions, however, were found to interfere even when present in minute quantities.

The molar composition of titanium (IV)-oxine N-oxide complex, determined by the modified method of continuous variations<sup>2</sup> was found to be 1:2 at pH 2.0 as well as at pH 4.0 (in presence of 0.001 M sodium acetate, no mixed ligand complexes being detected in the system) at 385-440 m $\mu$ . These results were also confirmed by Asmus's straight line method<sup>3</sup> and by the logarithmic method of Bent and French.<sup>4</sup>

The pK<sub>a</sub> of oxine N-oxide in aqueous solutions was spectrophotometrically found to be  $9.3 \pm 0.1$  at 25°C. The equilibrium constant K for the reaction



as determined by (a) Harvey and Manning's method,<sup>5</sup> (b) Foley and Anderson's method,<sup>6</sup>

and (c) Asmus's method<sup>3</sup> was found to be  $(4.0 \pm 1.8) \times 10^5$  at pH  $3.5 \pm 0.1$  in aqueous medium at 25° C. The stability constant ( $\beta_2$ ) of the complex determined by the above-mentioned methods as well as from the Bjerrum's formation curves obtained spectrophotometrically<sup>7</sup> was found to be as  $\log \beta_2 = 17.2 \pm 0.2$  in aqueous medium at 25° C.

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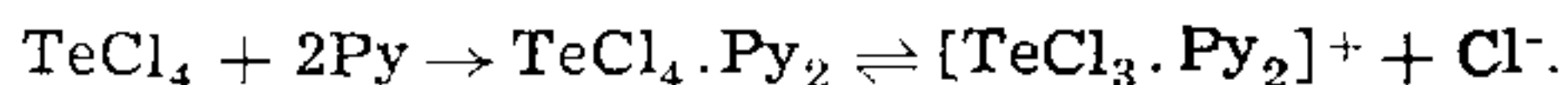
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### IONIC ADDUCTS OF AMIDES

MUCH interest has been shown in the donor properties of amides and a large number of donor-acceptor complexes with Lewis acids have been isolated. N.m.r. studies of the solutions of amides in fluorosulphuric acid<sup>1</sup> have proved conclusively that the amide donation is through the carbonyl oxygen rather than through the nitrogen atom as was previously visualised.<sup>2</sup> Infra-red spectral analysis<sup>3,4</sup> also supports the donor character of carbonyl oxygen and these complexes have been found to be non-ionic in nature. In the case of non-stoichiometric complexes of composition  $\text{SnCl}_4 \cdot 4\text{CH}_3\text{CONH}_2$ , the excess of the amide molecules are attached to the complex through hydrogen bonding and from conductance studies in acetic acid it has been concluded that these complexes are protonic in nature.<sup>5</sup>

Tellurium tetrachloride has been found to be ionic in the solid<sup>6,7</sup> and molten states.<sup>8</sup> Infra-red spectral analysis of its complexes with bases<sup>9</sup> suggests that they are ionic in nature as



We have isolated a number of complexes of tellurium tetrachloride with amides and substituted amides, and in this communication report their ionic nature.

The complexes of tellurium tetrachloride with amides, e.g., acetamide, N-methyl acetamide, dimethyl acetamide, N-methyl formamide, formamide and dimethyl formamide have been isolated in dry benzene and their stoichiometric compositions have been established from the elemental analyses (Table I). Infra-red spectra of pure amides undergo a significant change on complex formation. Though we have recorded the I.R. spectra of all these complexes, yet for brevity discussion shall be limited to the spectrum of tellurium tetrachloride-acetamide adduct.

The amide-1 band which is due to carbonyl stretching frequency at  $1685 \text{ cm}^{-1}$  is displaced to a lower spectral region, i.e.,  $1650 \text{ cm}^{-1}$  indicating the donor character of the carbonyl oxygen of the amide. A slight increase in the stretching vibrations of N-H band from  $3445 \text{ cm}^{-1}$  to  $3455 \text{ cm}^{-1}$  and that of C-N band from  $1410 \text{ cm}^{-1}$  to  $1440 \text{ cm}^{-1}$  also confirms that tellurium tetrachloride has combined with acetamide through carbonyl oxygen. For a weaker Lewis acid like tellurium tetrachloride, the shift in the amide band, though small, is quite significant and indicates complex formation.

Far infra-red spectral analysis of this adduct shows a broad band at  $240 \text{ cm}^{-1}$  which is slightly resolved. This is a characteristic absorption band for five co-ordinate tellurium.<sup>10</sup> The lowering of Te-Cl frequency (pure  $\text{TeCl}_4$ , Te-Cl  $360 \text{ cm}^{-1}$ ) is because of the increase in the co-ordination number of tellurium from

TABLE I

Amide used	Stoichiometric composition $\text{TeCl}_4$ : Amide	Colour	Analysis			
			Required % Te	Found Te	Required % Cl	Found Cl
1. Acetamide	.. 1 : 2	Yellow solid	32.86	32.92	36.50	36.30
2. N-methyl acetamide	.. 1 : 2	"	30.71	30.76	34.14	32.67
3. Dimethyl acetamide	.. 1 : 2	Yellow viscous liquid	28.76	28.37	32.02	32.00
4. N-methyl formamide	.. 1 : 2	Yellow semi-solid	32.98	32.86	34.17	34.12
5. Formamide	.. 1 : 2	"	35.48	35.42	39.49	38.67
6. NN-dimethyl formamide	.. 1 : 2	Yellow solid	30.71	30.16	34.14	34.09