stant of Cu (II)—1-nitroso 2-naphthol is greater than that of UO₂—1-nitroso 2-naphthol; on the contrary Jefurkar et al.¹¹, observed a stability order UO₂ (II) > Cu (II). In the present investigations the stability order of Cu (II) > UO₂ (II) in case of 2-nitroso 1-naphthol chelates and Cu (II) < UO₂ (II) in the case of 2-nitro 1-naphthol chelates. In this context Back¹² has rightly pointed out that the natural stability order of Irving-Williams is probably valid only for the high spin complexes and the stability order might even become less defined with oxo cations. The low stability of the metal chelates of 2-nitro 1-naphthol as compared with 2-nitroso 1-naphthol chelates is due to the fact that the oxygen of a resonating nitro group is weaker basic centre than the oxygen of the nitroso group.

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7. Hoffman, O., Ber., 1885, 18, 46.

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VINYL POLYMERIZATION BY THALLIUM (III) SALTS

The mechanism of oxidation of organic substrates by thallium salts has been fairly well established. Little is known about the reaction of thallium with radicals. But for a solitary report there has not been much evidence for the reaction between Th (III) and any free radical. The use of thallium (III) salts as polymerization catalyst has been scant. A few patents have been obtained on the gas phase olefin polymerization. However the use of thallium (III) salts as catalysts for vinyl polymerization in solution has not been reported till now. For the first time the present study reports several interesting aspects of thallium (III) acetate catalyzed polymerization of acrylic amide.

Thallium (III) acetate is a fairly efficient initiator causing a 50% conversion in 30 minutes at a temperature of 50° C. The rate of acrylic polymerization was found to be directly proportional to the monomer concentration (vide Fig. 1). Another interesting feature which was observed was that the rate of polymerization remained constant with change in the metallic salt concentration, even when the thallium (III) acetate concentration was changed hundredfold, viz, from 5 x 10⁻⁶ to 5 x 10⁻⁸ M. The rate of decomposition of the thallium (III) acetate however varied linearly with the concentration of the metallic salt indicating the possibility of simultaneous reaction paths available for the thallium (III) salt (vide Fig. 1). Chain

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Fig. 1. Effect of Monomer concentration and metal concentration on Rates: T = 50° C; t = 30 min, A₁ = d [M]/dt x 10⁻⁴ vs. [M]; B₁ = d [I]/dt x 10⁻⁵ vs. [I] x 10⁻⁵.

determination by the thallium (III) acetate is postulated to explain the kinetics.

\[ \text{Tl(OAc)}_3 \rightarrow \text{Tl(OAc)} + 2 \text{AcO}^\circ \]

\[ \text{AcO}^\circ + \text{M} \rightarrow \text{M}^\circ \]

\[ \text{M}^\circ + \text{M} \rightarrow \text{M}_n^\circ \]

\[ \text{M}_n^\circ + \text{Tl(OAc)}_3 \rightarrow \text{polymer} \]
Assuming the steady state conditions and assuming \( k_p \) and \( k_f \) to remain constant and independent of chainlength the following expressions are derived:

\[
-\frac{d[M]}{dt} = k_d k_p [M]
\]

and

\[
-\frac{d[I]}{dt} = 2 k_d [I]
\]

A similar feature was observed in the photopolymerization of methacrylamide by trans-diazidotetramminecobalt (III) azide\(^6\) and in the photopolymerization of N-vinylpyrrolidone by azidotetramminecobalt (III) chloride\(^7\), wherein termination by the excited complex molecule was postulated. The rate constants calculated were \( k_2 = 2.18 \times 10^{-4} \) sec\(^{-1}\) and \( k_p/k_f = 1.25\). The unusually low \( k_p/k_f \) value may be explained by the high termination constant for thallium (III) acetate.

Another interesting aspect found was that thallium (III) acetate is an excellent photoinitiator of vinyl polymerization; as a matter of fact the efficiency being much more photochemically than thermally. Further work is in progress to unravel the ramifications of the kinetics.

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SYNTHESIS OF SUBSTITUTED 2-ANILINO-BENZOXAZOLES

Benzoazoles have been reported to demonstrate diverse biological properties\(^1\text{-}^5\). Some 3-substituted benzoazolineones synthesised and screened by us have also shown antibacterial activity\(^3\text{-}^5\). Syntheses of certain substituted 2-anilinobenzoazoles (I) for biological screening have been given in this note.

For the synthesis of (I), 2-chlorobenzoxazole and aromatic amines in equimolar proportions were allowed to react in anhydrous benzene. 2-(4'-carboxethoxyanilino) benzoazole (Ia) obtained from methyl\(^4\) aminobenzosate and 2-chlorobenzoxazole has been hydrolysed to the corresponding carboxylic acid (Ie). 1e was also obtained when 2-chlorobenzoxazole and 4-aminobenzoic acid were heated together. The product (Ij) synthesised from 4-aminoacetophenone has been smoothly reduced to the corresponding secondary alcohol (Ik) with sodium borohydride. The infrared spectrum of Ik showed characteristic absorption peaks at 3270 cm\(^{-1}\) (NH) and 1678 cm\(^{-1}\) (C=O). Reduction of Ij to Ik caused the disappearance of carbonyl absorption from the i.r., of Ik; an additional band was observed at 3077 cm\(^{-1}\) (OH, broad) besides band at 3279 cm\(^{-1}\) (NH).

\[
\text{I} \\
\begin{array}{c}
\text{N} \\
\text{H} \\
\text{C}_6\text{H}_5 \\
\end{array}
\]

Biological Data.—All the compounds described in Table I were screened for their inhibitory effects against four microorganisms: Staphylococcus aureus, Escherichia coli, Salmonella typhi, and Bacillus megaterium by agar diffusion technique\(^6\). None of the compounds showed any significant activity.

Experimental

Melting points were determined in open capillaries and are not corrected. Infrared spectra were recorded on a Perkin-Elmer 337 Spectrophotometer in KBr.

Substituted 2-Anilinobenzoazoles (I)—2-Chlorobenzoxazole (0.01 mole) and a suitable aromatic amine (0.01 mole) were suspended in 50 ml of dry benzene and refluxed for three hours. The contents assumed a light pink colour which slowly faded away as the reaction progressed. Excess of benzene was distilled off and the solid product thus obtained was recrystallised from ethanol. The analytical and other pertinent data are recorded in Table I.

Reduction of 2-(4'-Acetylaminino) Benzoazole (Ij) to (Ik) with Sodiumborohydride.—To a solution of Ij (0.50 g) in ethanol was added gradually 0.2 g. of Na\(_2\)BH\(_4\) dissolved in ethanol and the mixture heated on a waterbath for 1 hr. and the excess of ethanol distilled under reduced pressure;