

computer facility and the total to K-shell photo-electric cross section ratios at the respective K-edges in the elements are deduced. In the present note, a study of the Z-dependence of these ratios is made using the measured values.

The measured ratios are fitted to a polynomial expression using the IBM 1130 computer. The best fit is obtained as:

$$T/K = 1 + 7.819 \times 10^{-3} Z - 1.8 \times 10^{-4} Z^2 + 7.625 \times 10^{-7} Z^3.$$

The values obtained from this expression are plotted in Fig. 1 alongwith those for the expressions of Allen<sup>3</sup> and Hubbell<sup>4</sup> and the recent theoretical values of Scofield.

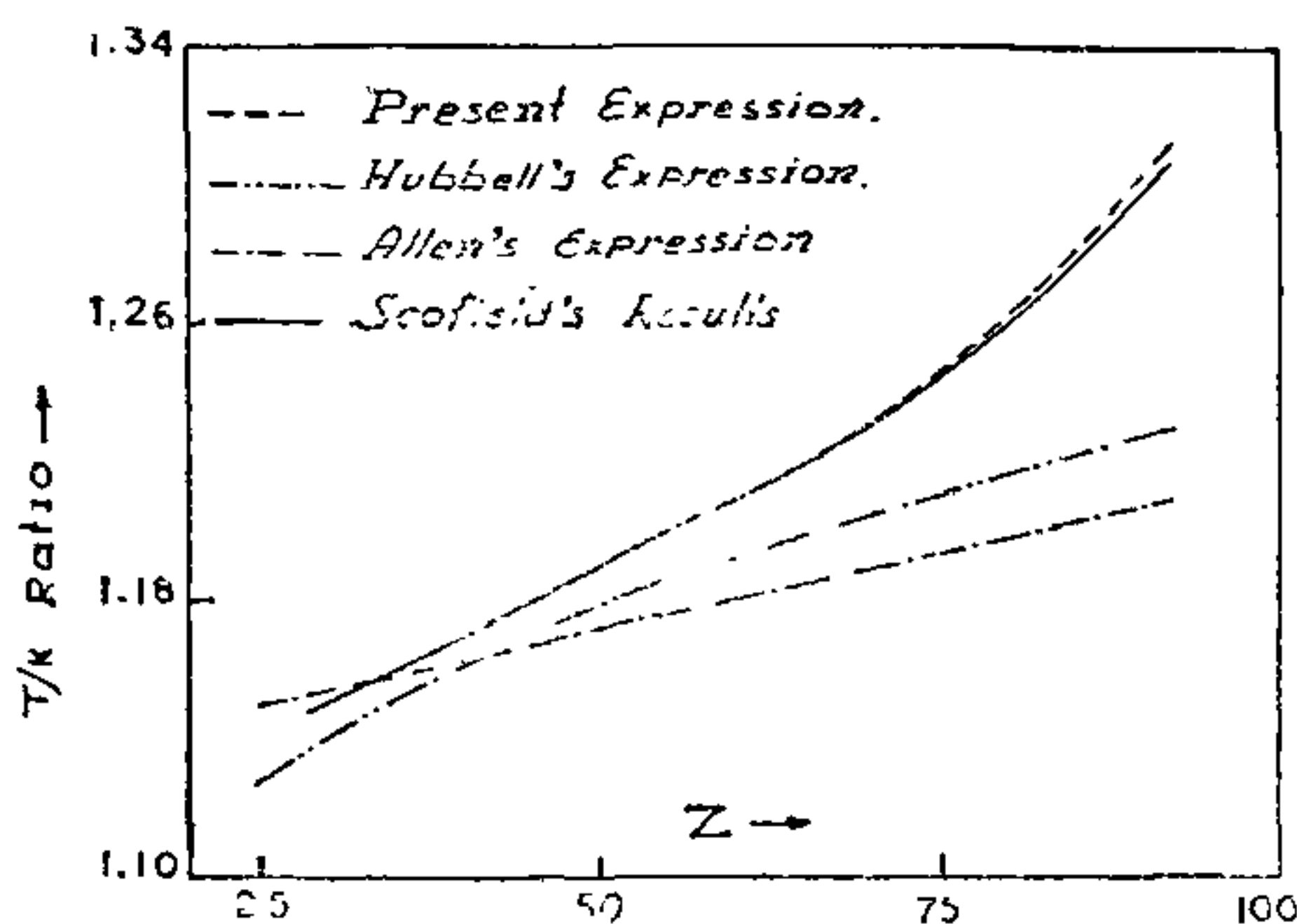


FIG. 1

It can be seen from the figure that the present trend differs from those of Allen and Hubbell in the high Z-region significantly. It can also be seen that the present values are in excellent agreement with the recent theoretical values of Scofield.

The Laboratories for V. RADHA KRISHNA MURTY.

Nuclear Research, K. SIVA SANKARA RAO.

Andhra University, J. RAMA RAO.

Waltair, India, K. PARTHASARADHI.

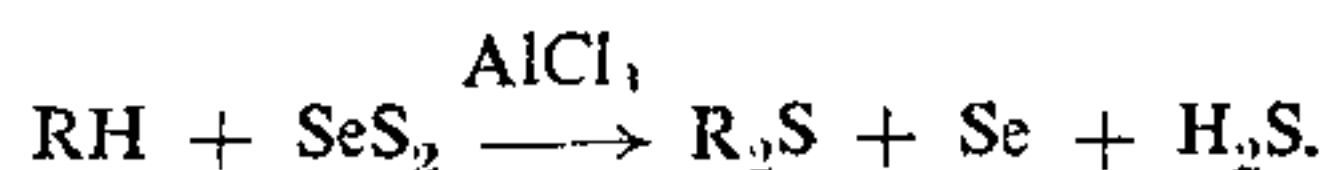
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## FRIEDEL-CRAFTS REACTION OF SELENIUM SULPHIDE

NUCLEOPHILIC addition of sulphur into the organic moiety under Friedel-Crafts condition is known only in the case of benzene<sup>1</sup> while addition of selenium under similar conditions towards the synthesis of diaryl selenides has not been reported. The ditolyl and xylyl sulphides are synthesised by reduction of sulfoxides<sup>2</sup> or by the reaction of diorganomercury compounds with sulphur<sup>3</sup> or from the reaction of lead salts of organothio compounds with aryl halides<sup>4</sup>. The methods of introducing selenium into the organic moiety are summarised in literature<sup>5-6</sup>. It would be desirable to have the synthesis of both diaryl sulphide and selenide in one step and towards this end selenium sulphide as a starting material offers an advantage.

In the course of our studies on the synthesis and reactivity of selenium sulphides it has been found that octatomic species,  $\text{Se}_8$ , are inert towards many reactions though they possess interesting structures. The selenium sulphide,  $\text{SeS}_2$ , synthesised by published method<sup>7</sup>, undergoes a variety of reactions and we wish to report here some of our results. The  $\text{SeS}_2$  reacts with benzene, toluene and *p*-xylene in presence of anhydrous  $\text{AlCl}_3$  to form diaryl sulphides in nearly quantitative amounts. No undesirable disulphide formation has been noticed. The course of the reaction can easily be monitored by the evolution of  $\text{H}_2\text{S}$  and quantitative precipitation of elemental selenium is observed at the completion of the reaction. The products are found to be pure from their bp/mp, elemental analysis, chromatographic and spectral methods. The reaction can be represented as:

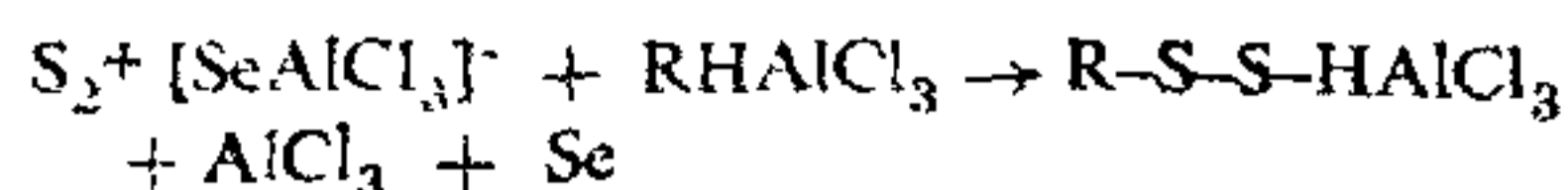


No formation of diaryl selenides has been noticed though different reaction conditions such as varying mole proportions of the reactants, reaction time and temperature are employed.

In the case of toluene the GLC data showed that the product contained a mixture of three isomers. The major component (53%) has been characterised as the *para* substituted derivative since the infrared spectrum showed two absorptions at 1890 and 1780  $\text{cm}^{-1}$ <sup>8</sup>. The minor components (35% and 12%) in the product, however, could not be identified by spectroscopic method nor the separation of the isomers was possible on account of their close boiling points. The minor components are recognised as di *ortho* and *ortho-para* substituted sulphides based on reactivity considerations.

The reaction seems to proceed through the formation of a reactive intermediate complex of the type,

$S_2^+ [SeAlCl_3]^-$ . This complex undergoes subsequent reactions as shown below :



The composition of the complex gains support from the mass spectrum of  $SeS_2$  which shows the predominant molecular ion being  $S_2^+$ . Further the postulation of such a complex also explains the nonformation of diaryl selenides owing to the poor nucleophilicity of selenium. The present work affords an elegant method towards the synthesis of simple diaryl sulphides in nearly quantitative yields.

#### Materials and Methods

All the chemicals used are of Analar grade and the solvents are distilled and dried before use. The infrared spectra are recorded on Perkin Elmer 237-B Infrared Grating Spectrometer. The GLC of diphenyl and tolyl sulphides are taken on 2-5% DC-11 silicone grease column at 150° and 174° respectively. The mass spectrum is recorded on MS 702 spectrometer using electron bombardment for molecular fragmentation.  $SeS_2$  was synthesised<sup>7</sup> by the reaction of aqueous solutions of selenious acid with  $Na_2S$  at 5-7° and used without purification.

**Diphenyl sulphide :** About 20 g of anhydrous  $AlCl_3$  was introduced into a three-necked flask containing 300 ml of benzene fitted with a stirrer, condenser and an addition flask containing 10 g  $SeS_2$ . The addition of  $SeS_2$  was done slowly under an atmosphere of nitrogen and the reaction commenced immediately with the evolution of  $H_2S$ . The reaction was completed in about 2 hrs. The reaction mixture was hydrolysed with ice and the solvent removed under reduced pressure. This left behind a pale yellow liquid and it was passed through a column of silica gel to remove any possible disulphides. The product was distilled under vacuum and the pure colourless liquid distilling at 162-163°/18 mm was collected. Yield : 90%. Similar procedure was adopted for the synthesis of ditolyl, and dixylyl sulphides. Di *p*-tolyl sulphide was obtained as colourless liquid boiling at 179-180°/11 mm. Yield : 80%. Di *p*-xylyl sulphide was obtained as colourless crystals, m.p. 75-76°. Yield : 80%.

One of the authors (A. D.) is thankful to NCERT, New Delhi, for the financial assistance,

Department of Chemistry,  
Indian Institute of Technology,  
Bombay, and

Department of Inorganic and  
Physical Chemistry,  
Indian Institute of Science,  
Bangalore 560 012, July 9, 1976.

A. DATTA.

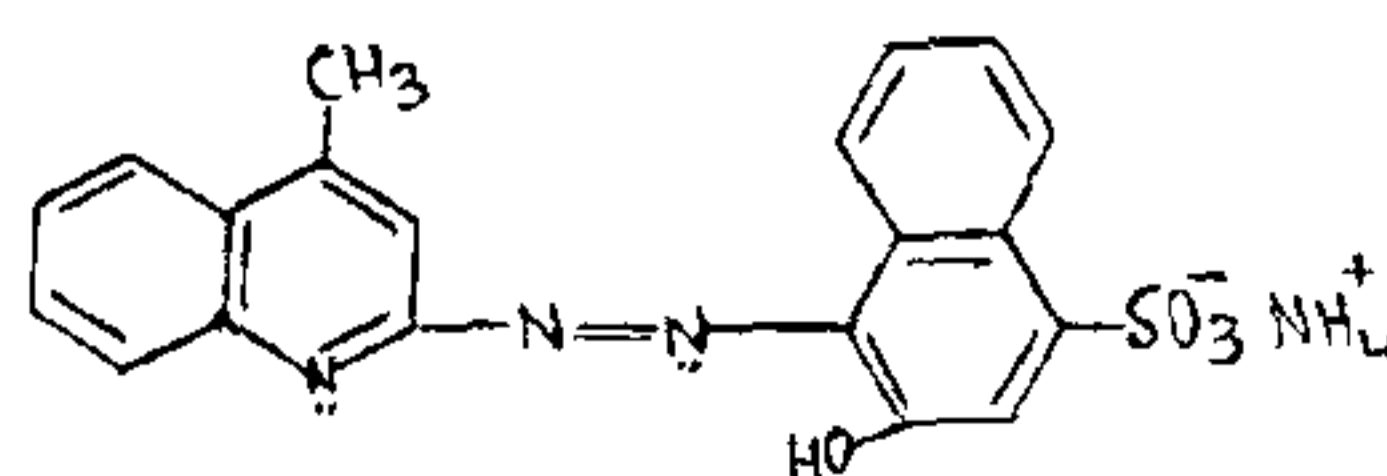
V. KRISHNAN.\*

\* Author to whom correspondence should be addressed at the latter address.

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#### ANALYTICAL POTENTIALITIES OF A NEW HETEROCYCLIC AZO DYE: 1-(2-LEPIDYLAZO)- 2-NAPHTHOL-4-AMMONIUM SULPHONATE (LANAS) AS A METALLOCHROMIC INDICATOR FOR TITRIMETRIC DETERMINATION OF MERCURY (II) WITH EDTA

HETEROCYCLIC azo dyes introduced recently<sup>1</sup> find intensive applications in analytical chemistry for micro determinations of metal ions spectrophotometrically<sup>2</sup> or complexometrically<sup>3-5</sup>. Only very few water soluble heterocyclic azo dyes have been explored so far as analytical reagents for micro determination of metal ions. In this communication, a new water soluble heterocyclic azo dye, 1-(2-lepidylazo)-2-naphthol-4-ammonium sulphonate (LANAS) has been synthesised, characterised and used as metallochromic indicator for complexometric determination of mercury (II).



(I)