

42 out of which 29 are a' and 13 are of a'' . All are allowed in infrared and Raman spectra.

The assignments of fundamental frequencies have been made on the basis of comparison with those of similar molecules like ethylene¹⁰ ($H_2C=CH_2$) benzene¹¹ and styrene.⁷ In addition, assistance has also been taken from the assignment of the three isomeric chloro- and bromostyrenes.¹²⁻¹³

The assignment of fundamental frequencies of β -bromostyrene is given in Table I.

TABLE I
Infrared absorption spectrum of β -bromostyrene

| Infrared (cm. ⁻¹) | Intensity | Assignment |
|-------------------------------|-----------|--|
| 690 | 9 | a'' C—C—C o.p. bending |
| 734 | 10 | a'' C—H o.p. bending |
| 770 | 5 | do. |
| 835 | 3 | do. |
| 912 | 3 | do. |
| | | (in CH : CHBr group) |
| 940 | 10 | a'' C—H o.p. bending |
| 983 | 2 | do. |
| 1006 | 2 | a' C—C stretching (ring breathing) |
| 1030 | 3 | a' C—H i.p. bending |
| 1071 | 4 | do. |
| 1158 | 2 | do. |
| 1186 | 4 | do. |
| 1221 | 8 | a' C—X stretching |
| 1280 | 3 | a' C—H i.p. bending |
| 1297 | 2 | a' C—H wagging (in CH : CHBr group) (Methylenic wagging frequency) |
| 1323 | 4 | a' C=C stretching |
| 1448 | 6 | a'' C—H scissoring mode (CH ₂ vib.) |
| 1490 | 5 | a' C=C stretching |
| 1570 | 5 | do. |
| 1600 | 7 | do. |
| | | (ethylenic group frequency) |
| 2800 | 2 | a' C—H stretching (in CH : CHBr group) |
| 3014 | 6 | a' C—H stretching |

o. p. = out-of-plane, i. p. = in-plane, X = CH : CHBr group.

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PREPARATION OF *m*-PHENYLENEDIISOTHIOCYANATE

m-PHENYLENEDIISOTHIOCYANATE is a useful intermediate in the preparation of certain interesting heterocyclic compounds.¹ It also finds applications as an antiseptic, an insecticide, and in some drug preparations. Billeter and Steiner² prepared it by the reaction³ of thiophosgene ($CSCl_2$) on *m*-phenylenediamine. Another method, patented in United States, describes its preparation by heating *m*-phenylenediisocyanate with phosphorus pentasulphide in an inert solvent. The former method is considered to be the most convenient one, and is generally preferred^{1,5} but because of the very high cost of thiophosgene, the method is not of common use. The latter method is also of little importance as it involves the use of an extremely rare chemical, *m*-phenylenediisocyanate. There is another method,⁶ available for the preparation of the isomeric compound, *p*-phenylenediisothiocyanate, involving the reaction of *p*-phenylenediamine with carbon disulphide and ammonia, isolating the corresponding bis-dithiocarbamate, treating it with sodium chloroacetate, and finally decomposing the product at pH 7, by zinc chloride. We report here the application of this method, with some modifications, to the preparation of *m*-phenylenediisothiocyanate, in fairly high yields.

Procedure.—A mixture of 20 g. (0.18 mole) of *m*-phenylenediamine, 40.3 g. (32 ml.; 0.53 mole) of carbon disulphide, 63 g. (70 ml.; 3.7 mole) of concd. aq. ammonia (sp. gr. 0.9), and 40 ml. of water, cooled with ice-cold water, was stirred mechanically for 2 hr. at 20–25° C. A thick precipitate of ammonium-*m*-phenylene-bis-(dithiocarbamate), dark brown in colour was obtained. It was filtered (unwashed), suspended in 60 ml. of water and treated with stirring, with 35 g. (0.3 mole) aq.

sodium chloroacetate at $\approx 25^\circ\text{C}$. and pH 7. The mixture containing ammonium-*m*-phenylene-bis-(*S*-carboxymethyldithiocarbamate) was allowed to stand for 1 hr. An aq. solution of 52 g. (0.38 mole) anhydrous zinc chloride (or chloride of a heavy metal having a standard potential between + 0.14 to + 1.1, e.g., Fe, Mn, Sn, etc.) was then added gradually with vigorous stirring. A precipitate of zinc-*m*-phenylene-bis-(*S*-carboxymethyldithiocarbamate) that formed, was immediately decomposed by the simultaneous addition of 4N NaOH at such a rate as to maintain pH ≈ 7 . The *m*-phenylenediisothiocyanate was recovered from the mixed reaction products by extracting thrice with 100, 50, and 35 ml. portions respectively of acetone. Evaporation of the solvent, and recrystallisation of the product from acetone furnished pale yellow needles of the diisothiocyanate (26 g.), m.p. 55° (lit.⁵ 55.5° , pet. ether). The product was also identified by preparing its derivative, *m*-phenylene-di-(1-tetrazoline-5-thione),¹ m.p. 178° (lit. 179°).

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ADSORBABILITY OF ORGANIC MOLECULES AT Hg/AQUEOUS M/10 SODIUM SULPHATE INTERPHASE

THE work of Barradas *et al.*³ indicates that the value of 'K', the adsorption coefficient as defined by Blomgren *et al.*¹ and ' β ' the adsorption index as used by Laitenen and Moisier² are in close agreement. Hence it can be concluded that for the analysis of the behaviour of the adsorbates at metal-electrolyte interphase it is sufficient to consider either of the two quantities. The adsorption coefficient 'K' ($\text{cm}^3 \text{mole}^{-1}$) can be obtained from the equation given by Blomgren *et al.*¹ as

$$\Gamma_A / (\Gamma_m - \Gamma_A) = KC_A \quad (1)$$

where C_A is the concentration of adsorbate in mole cm^{-3} , Γ_A is the surface excess of the adsorbate and Γ_m is its experimentally observed highest value of surface excess.

Four B.D.H. AnalAR compounds, viz., methanol, allyl alcohol, dioxan and phenol have been studied using dropping mercury electrode (DME) in aqueous M/10 sodium sulphate solution at 25.0°C . Concentration of the organic compounds was varied from 0.01 to 0.50 M. Electrocapillary data were obtained from accurate determination of drop times of a DME. Sargent capillaries were employed. The drop times measured by an electronic drop counter were accurate upto 0.001 sec. Corbusier and Gierst equation⁴ was employed to convert the drop times into the interfacial tension values. The potential on the DME was altered in steps of 0.5 volt in the range -0.1 to -1.5 volt measured against a normal calomel electrode with a Cambridge Pye potentiometer. The Γ_A values were computed using the expression (which can be derived from the Gibbs adsorption isotherm)

$$(\partial \nu / \partial \mu)_E = -\Gamma_A$$

where ' ν ' is the interfacial tension, ' μ ' is the chemical potential of the adsorbate, and 'E' is the polarising potential on the DME. The adsorbabilities in terms of the adsorption coefficient 'K' ($\text{cm}^3 \text{mole}^{-1}$) have been evaluated and written in Table I.

TABLE I

Adsorbabilities of organic substances on mercury at the point of zero charge in terms of 'K' ($\text{cm}^3 \text{mole}^{-1}$) for different surface coverages ($\theta = \Gamma_A / \Gamma_m$) a, b, c and fixed concentration (C_A) d

| Substance | 'K' for $\theta=0.10$ (a) | 'K' for $\theta=0.25$ (b) | 'K' for $\theta=0.50$ (c) | 'K' for $C_A=0.10\text{M}$ (d) |
|---------------|---------------------------|---------------------------|---------------------------|--------------------------------|
| Methanol | 0.44×10^4 | 0.39×10^4 | 0.52×10^4 | 0.40×10^4 |
| Allyl alcohol | 0.27×10^4 | 0.41×10^4 | 0.62×10^4 | 0.48×10^4 |
| Dioxan | 0.48×10^4 | 0.48×10^4 | 0.93×10^4 | 0.82×10^4 |
| Phenol | 1.10×10^4 | 1.58×10^4 | 2.43×10^4 | 0.98×10^4 |

It is seen from Table I that a regular trend in the degree of adsorbability which is related to the physical properties of the adsorbates is obtained when 'K' values are compared for constant surface coverage or for constant concentration, e.g., phenol has the highest 'K' as also density and molecular weight among the compounds investigated. For the same concentration or for the same surface coverage of adsorbates (methanol, allyl alcohol, dioxan and phenol) the adsorbability at the point of zero charge decreases in the order (cf. Table I).

Phenol > Dioxan > Allyl alcohol > Methanol.