

(4.28), 294 (4.5), IR, KBr (cm^{-1}) (1663(s), 1590(s), 1550(m), 1280(s)). Similarly, 4-hydroxy-7,8-dimethylcoumarin [II, m.p. 236–37°, UV $\lambda_{\text{max}}^{95\% \text{ EtOH}}$ (log ϵ) 239 (4.32), 289 (4.51), IR, KBr (cm^{-1}) 1650(s), 1600(s), 1550(s), 1250(s)] was obtained from 2,3-xyleneol, 6-chloro-4-hydroxy-7-methylcoumarin [III, m.p. 229–30°, UV $\lambda_{\text{max}}^{95\% \text{ EtOH}}$ (log ϵ) 238 (4.21), 307 (4.42), IR, KBr (cm^{-1}) 1630(s), 1600(s), 1300(m), 1250(m)] from 4-chloro-3-cresol and 4-hydroxy-8-phenylcoumarin [IV, m.p. 236–37°, UV $\lambda_{\text{max}}^{95\% \text{ EtOH}}$ (log ϵ) 243 (4.42), 296 (4.44), IR, KBr (cm^{-1}) 1680(s), 1600(s), 1280(s), 1240(s)] from 2-hydroxybiphenyl.

Since Anschütz² reported the first synthesis of 4-hydroxycoumarin, several methods have been developed for the syntheses of 4-hydroxycoumarin derivatives³. The method of Shah *et al*¹ of condensing phenols with malonic acid in presence of phosphoryl chloride and anhydrous zinc chloride appears to be the most convenient single-step synthesis from phenols, giving fairly good yields.

All the 4-hydroxycoumarins were brominated (bromine in acetic acid, 30°), nitrated (concentrated nitric acid in acetic acid, 100°), sulphonated (chlorosulphonic acid in dioxane, 30°) and coupled with phenyldiazonium chloride. 4-Hydroxy-5,7-dimethylcoumarin (I) gave 3-bromo (m.p. 172°), 3-nitro (m.p. 168°), 3-sulpho (m.p. 240°) and 3-phenylazo (m.p. 207°) derivatives. Similarly the corresponding 3-bromo (m.p. 170°), 3-nitro (m.p. 164°), 3-sulpho (m.p. 225°) and 3-phenylazo (m.p. 216°) from II, 3-bromo (m.p. 157°), 3-nitro (m.p. 164°), 3-sulpho (m.p. 210°) and 3-phenylazo (m.p. 204°) from III and 3-bromo (m.p. 230°), 3-nitro (m.p. 203°), 3-sulpho (m.p. 227°) and 3-phenylazo (m.p. 190°) from IV were obtained.

Elemental analyses of all the compounds agreed with the expected structural formulae.

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INFRA-RED IDENTIFICATION OF Fe-S BOND IN ASSAM COAL

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THE bondings of organic sulphur in high sulphur Assam coal has been known as C-S linkage. Thiophenol, disulphide and thiophene have been reported as components of organic sulphur¹. The nature of sulphur bondings are very important from the viewpoints of desulphurization and liquefaction and also in understanding the constitution of high sulphur coal; this study has therefore been carried out. As x-ray photoelectron spectroscopy normally does not provide structural information of organic sulphur in Assam coal², IR technique was used to examine such structural components.

As regards minerals occurring in coal, Estep *et al*³ have identified the IR absorption bands of pyrite and marcasite as:

pyrite – 284(w), 340(m), 391(vw), 406(s) cm^{-1}
marcasite – 285(w), 321(m), 350(m), 396(s), 407(s), 422(vw) cm^{-1} .

Both these minerals exhibit two common bands (nearly 400 cm^{-1}) and the only difference between them is that pyrite shows an unique band at 340 cm^{-1} .

The absorption band in the region 600–200 cm^{-1} in the spectrum of Assam coal has not been evaluated earlier. Therefore a high sulphur coal sample ($c = 80.7\%$) containing 0.6% pyrite and 2.0% organic sulphur was taken and treated with warm dilute (2N) nitric acid to remove sulphate and pyrite sulphur⁴. The acid-washed coal sample was then subjected to x-ray investigation to determine whether any pyrite is present. The IR spectrum of this sample was recorded in KBr pellet using a Perkin-Elmer model 521 spectrophotometer in the range 4000–200 cm^{-1} .

Careful investigation of IR spectrum reveals two broad absorption bands (at 340 and 540 cm^{-1}) in the region 600–200 cm^{-1} . Absence of 400 cm^{-1} band in the spectrum indicates the absence of pyrite and marcasite in the sample.

The major part of the organic sulphur in Assam coal has been reported to contain SH groups⁵. During sample preparation, no changes occurred in the SH group as nitric acid would not attack the organic sulphur⁶. No absorption band is observed for S-H stretching vibration which otherwise occurs in the

region $2600\text{--}2500\text{ cm}^{-1}$. Moreover, no absorption band appears at 485 cm^{-1} assignable to S–S stretch thus suggesting that sulphur is linked to metal resulting in metal-sulphur bond formation. Further, the band at 2300 cm^{-1} , characteristic of metal bonded to SH groups, is absent revealing that the SH groups get deprotonated while forming metal-sulphur bond.

Although bondings of organic bound or non-pyritic iron have been studied^{7–9} no work seems to have been done on high sulphur Assam coal. After washing the inorganic sulphur with dilute nitric acid, the sample on ashing (at 800°C) shows the presence of iron¹⁰ which is organically bonded to the coal molecule. Therefore, the bands at 340 and 540 cm^{-1} are most probably due to the contribution of Fe–S and Fe–O stretching vibrations respectively. The Fe–O bond formation is due to the linkage of oxygen containing functional groups such as carboxyl, hydroxyl, carbonyl etc groups of organic matter constituting the coal, with iron.

The following reasons are advanced for the formation of Fe–S bond in coal: (i) Iron is the dominant metal in peat¹¹ and can exist in solution at neutral pH¹². Sulphur containing amino acids present in living plants and microorganisms or from diagenetic processes is known to occur in peat¹⁵. (ii) Occurrence of iron complex of sulphur containing amino acid in marine sediment¹⁴ resulting Fe–S bond formation; (iii) Formation of mixed-ligand complex of humic acid containing hydrosulphide (SH^-) as one of the ligands in peat bog¹⁵; (iv) Occurrence of metal-bonded sulphide organic matter complex in lake and marsh sediments¹⁶; (v) Sulphate-reducing bacteria are abundant in peat¹² and a metalloprotein (ferredoxin), containing Fe–S bond, has been isolated from them¹⁷. After the death of bacteria, they deposit along with the coal constituents. This is quite likely because microorganisms contribute at least 5–10% of peat organic matter¹⁸.

Assam coal is known as sub-bituminous or lignitous coal. In lignite, sulphur is not incorporated into a stable aromatic network¹⁹. Hence, the formation of co-ordination complexes in coal below the rank of bituminous coal is quite likely. The present results indicate that Fe–S moiety is, by far, the most abundant component of organic sulphur in Assam coal.

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