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CHEMISTRY

Extensive Reduction of Coal by a New Electrochemical Method

In recent years electrolytic methods have been used in the reduction and structural elucidation of coal¹⁻². The usefulness of these methods is limited by the fact that the benzene ring (that is, the isolated benzene ring as in benzene or tetralin), which may represent a large portion of the coal structure, has not previously been reduced electrolytically. Work here has shown that reduction of benzene can be achieved by electrolysis in ethylenediamine saturated with lithium chloride³. The same method has now been successfully applied to the reduction of a high-rank coal and has resulted in the addition of 44 hydrogens per 100 carbon atoms. The best electrochemical reduction achieved² prior to this was carried out in dimethylformamide and amounted to the addition of 14 hydrogens.

Six grams of the coal (Pocahontas vitrain ground to pass 325 mesh) suspended in 100 ml. of ethylenediamine containing 1.4 g of lithium chloride was electrolysed at 33° between carbon electrodes at 0.5 amp and 115 V. Apparatus and technique of electrolysis³ and recovery of the reduced coal⁴ were the same as described previously. Current efficiency at the beginning of the electrolysis was 46 per cent and dropped to 10 per cent after 15 h. The electrolysis was continued for an additional 15 h, during which time the current efficiency remained practically constant. The reduced coal was recovered from the solution in 95 per cent yield, analysed and subjected to a second and third electrolytic reduction; it was tan-grey in colour. Analyses of the original and reduced samples are shown in Table 1.

Table 1. ELECTROCHEMICAL REDUCTION OF POCAHONTAS NO. 3 VITRAIN

	Grams	C	H	N	S	Ash	H atoms added* per 100 C atoms in starting material
Original vitrain	—	87.66	4.22	1.06	0.65	2.45	—
First reduction	6.10	87.97	4.42	1.08	0.73	2.39	—
Second reduction	—	83.05	6.43	3.39	0.63	2.55	24.3
Third reduction	—	84.19	6.18	3.44	0.95	2.52	—
Original	5.80	80.72	6.95	4.47	0.36	2.47	32.4
First reduction	—	80.80	7.12	4.32	0.38	2.39	—
Second reduction	3.16	80.73	7.73	4.15	0.39	2.76	43.7
Third reduction	—	80.48	7.76	4.24	0.25	3.03	—

* Method of calculation as described in ref. 4.

The ratio of lithium chloride used to total hydrogen taken up by the coal was about 1 : 2. This ratio is much more favourable than that obtained in the chemical reduction of the same coal⁴ where the ratio of lithium metal to hydrogen added was 1 : 0.1. An interesting result is the fact that the solubility of the electrolytically reduced coal in pyridine at room temperature (74 per cent) is higher than that of the chemically reduced coal. In the latter case, 45 hydrogens were added but the solubility was only 63 per cent. It is conceivable that chemical reduction at elevated temperature, in contrast to electrolytic reduction at room temperature, is accompanied by polymerization resulting in a decrease in solubility. The advantage of ethylenediamine over dimethylformamide² is probably connected with the fact that ethylenediamine can solvate lithium. Experiments³ indicate that lithium acts as an electron transfer agent in the reduction of benzene in the ethylenediamine-lithium chloride system.

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Interaction of Methyl-substituted Borazines with Various Acceptor Molecules

It has been suggested that borazines might be expected to form molecular complexes with electron-pair acceptors¹, and interactions between hexamethylborazine and tetracyanoethylene² or iodine³ have been reported. In further support of this suggestion we wish to report the initial results of a spectrophotometric investigation of the interaction between methyl-substituted borazines and some acceptor molecules. Solutions of B-trimethyl-, B-trimethyl-N-methyl-, B-trimethyl-N-dimethyl-, and hexamethyl-borazine in carbon tetrachloride and in *n*-heptane exhibit featureless absorption spectra in the range 600–200 mμ, but the spectra of mixtures containing these borazines and typical acceptor molecules in the same solvents exhibit bands which are not characteristic of the acceptors. (See Table 1 for some representative data.)

Table 1. POSITIONS (mμ) OF NEW ABSORPTION BANDS EXHIBITED BY MIXTURES OF SOME METHYL-SUBSTITUTED BORAZINES AND VARIOUS DONORS*

	(Me) ₃ B ₃ N ₃ H ₃	(Me) ₂ B ₂ N ₂ H ₂ Me	(Me) ₃ B ₃ N ₃ H ₂ (Me) ₂	(Me) ₆ B ₃ N ₃ (Me) ₃
Iodine	290	289, 390	294, 390	291, 390
Picric acid	250†	260†, 433	258†, 455	258†, 455
<i>p</i> -Benzoquinone	none	335	335	335
Chloranil	none	345	350	345
Tetracyanoethylene	—	321	320	320

* 10 : 1 mole ratio of borazine to acceptor, at a concentration of 10⁻³ M.

† Shoulder.

The new bands appear in the spectral region in which charge-transfer bands for aromatic systems occur and can be attributed to molecular complexes formed between the borazine and the acceptors. It is noteworthy that complex formation involving B-trimethylborazine produces the smallest effect on the spectra of the free acceptor molecules, and that mixtures of B-trimethyl-N-methyl-, B-trimethyl-N-dimethyl-, or hexamethyl-borazine with the same acceptors exhibit substantially equivalent spectra. The spectra of iodine, sulphur dioxide, maleic anhydride, tetracyanoethylene, *p*-benzoquinone, picric acid, chloranil, and iodine monochloride are markedly affected by the addition of tetra-, penta-, or hexa-methyl-borazine; the last three named acceptors undergo a further slow reaction, and orange-coloured precipitates separate from mixtures containing picric acid on standing.