Extensive Reduction of Coal by a New Electrochemical Method

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In recent years electrolytic methods have been employed in the reduction and structural elucidation of coal (1, 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 in this laboratory has shown that reduction of benzene can be achieved by electrolysis in ethylenediamine saturated with lithium chloride (3). The same method has now been successfully applied to the reduction of a high rank coal and has resulted in the addition of 36 hydrogens per 100 carbon atoms. The best electrochemical reduction achieved (2) prior to this amounted to the addition of 14 hydrogens.

EXPERIMENTAL

Six grams of the coal (Pocahontas vitrain ground to pass 325 mesh) suspended in 100 milliliters of ethylenediamine containing 1.4 grams of lithium chloride was electrolyzed at 33° between carbon electrodes at 0.5 amperes and 115 volts. Apparatus and technique of electrolysis (3) and recovery of the reduced coal (4) were the same as described previously. Current efficiency at the beginning of the electrolysis was 46 percent and dropped to 10 percent after 16 hours. The electrolysis was continued for an additional 15 hours during which time the current efficiency remained practically constant. The reduced coal was recovered from the solution, analyzed and subjected to a second electrolytic reduction. The current efficiency at the beginning of the second electrolytic reduction was 20 percent and dropped to 8 percent after 16 hours. The electrolytis was continued for 15 hours during which time the current efficiency remained at 8 percent. Recovery of the reduced coal was 95 percent. The reduced coal was tan-gray in color and 73 percent soluble in pyridine; the solubility of the unreduced coal was only 3 percent. The analyses of the original and reduced samples are shown in Table 1. The ratio of total hydrogen taken up by the coal to lithium chloride used was about 2:1.

DISCUSSION

Perhaps the most interesting result is the fact that the solubility of the electrolytically reduced coal in pyridine at room temperature (73 percent) is higher than that of the same coal reduced chemically (4) with excess lithium in ethylenediamine at 90-100°. In the latter case, 45 hydrogens were added but the solubility was only 63 percent. 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.

REFERENCES

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TABLE 1. - Electrochemical reduction of Pocahontas vitrain

Substance	C	H	N	S	Ash	H atoms added[a] per 100 C atoms in starting material
Original vitrain	87.94	4.53	1.12	1.01	3.10	
	88.09	4.58	1.15	0.97	2.98	
First reduction	81.82	6.29	2.93	1.12	3.97	21.1
	81.77	6.15	3.29	1.21	3.76	
Second reduction	80.81	7.21	3.82	0.31	3.85	36.1
	80.73	7.19	3.80	0.51	3.21	

[a] Method of calculation as described in reference 4.