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Reduction of Coal by Lithium-Ethylenediamine. Studies on a Series of Vitrains.

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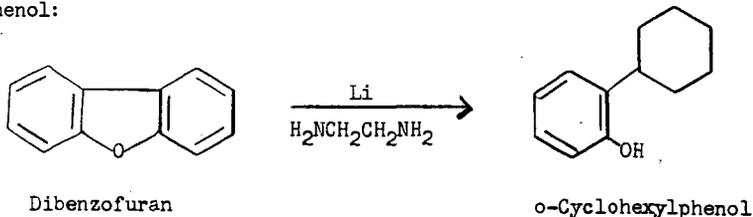
In an earlier report from this laboratory,^{1/} it was demonstrated that coals are reduced by lithium in ethylenediamine.^{2/} We now wish to present a more detailed study of the reduction of seven low-ash vitrains of varying ranks, and to describe the reduction of a graphite.

The reductions were carried out under closely controlled conditions, since it is known^{3/} that the amount of hydrogen added to a vitrain is to some extent a function of the experimental procedure. The starting materials are described in Table I. The analytical data on the starting materials and on the products of reduction are given in Table II. In Table III the analytical data for the starting and reduced materials are corrected to an ash-, sulfur-, and ethylenediamine-free basis. Table III also gives the amount of hydrogen added to the starting materials, expressed both as grams of hydrogen added per 100 g. of starting material and as atoms of hydrogen added per 100 carbon atoms in the starting material.

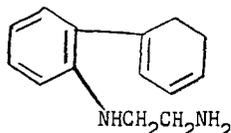
Figure 1 gives the hydrogen added as a function of carbon content. While the curve needs further definition, its general shape seems clear. The hydrogen uptake is low for lower rank coals, rises rapidly with increasing rank, reaches a maximum at about 90 percent carbon, and then falls sharply. A series of experiments with various polynuclear compounds leads to the formulation of a reasonable explanation of these results.

Several pure organic compounds were reduced with lithium in ethylenediamine (according to the usual procedure^{2/}); these were chosen because they contained certain structures known to be present in coal.

Diphenyl ether underwent cleavage of the ether linkage; the product was mainly phenol (83 percent), but small amounts of benzene (1 percent), cyclohexene (3 percent), cyclohexane and cyclohexanone were formed. It is significant that phenol was the major product although excess lithium was used; it is evident that the aromatic ring in phenol is not reduced easily by lithium-ethylenediamine. Further evidence for this effect was obtained with dibenzofuran; this compound yielded chiefly o-cyclohexylphenol:

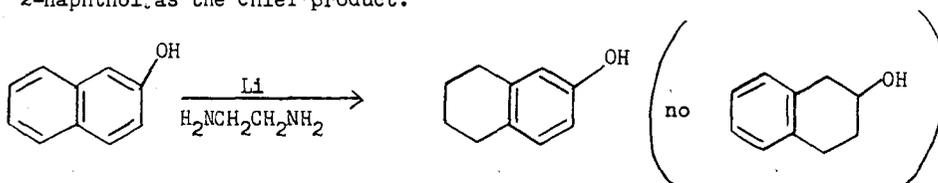


Again, the phenolic part of the molecule is resistant to reduction while the unsubstituted ring reduces easily. Another product formed in small amount was a solid material with the empirical composition $C_{14}H_{19}N_2Cl$; low-voltage mass spectrometric analysis of this material showed that the molecular weight corresponded to a monomer of this empirical formula. This may be the hydrochloride of an amine with a structure such as:



Although the structure is uncertain, this does suggest that ethylenediamine may add to coal by replacing certain oxygen functions with an $-NHCH_2CH_2NH_2$ side chain.

2-Naphthol was treated with lithium-ethylenediamine in the usual way; as expected, the unsubstituted ring was reduced most easily, giving 5,6,7,8-tetrahydro-2-naphthol as the chief product.



None of the secondary alcohol which would result from the reduction of the phenolic ring was found in the reaction products.

These examples show that the presence of a phenolic group on a benzene ring inhibits the reduction of that ring by the lithium-ethylenediamine system. This inhibition may be due to the formation of a lithium salt of the phenol which is then protected from further attack, or to the development of a negative charge on the phenol. Since reductions in metal-amine systems proceed by the addition of electrons, the negative charge would prevent the further addition of electrons to the ring.

On the other hand, it was possible to show that large polynuclear molecules, with no phenolic substituent, are reduced quantitatively by lithium-ethylenediamine. Coronene was reduced almost completely to the perhydro compound, as shown in Figure 5.

The shape of the curve in Figure 1 may now be explained, to some extent at least, in the following manner. Lower rank vitrains are relatively soluble in ethylenediamine, so that they are readily attacked by the reducing system. However, they contain fairly large amounts of oxygen, which is present almost entirely as either ether or hydroxyl; it is known^{2/} that these groups are relatively resistant to lithium reduction. The higher rank vitrains are less soluble, and thus less amenable to the reagent; but they contain only a small amount of oxygen. The higher rank vitrains also contain many more aromatic structures than the low rank. In the course of the reduction, the soluble, low rank vitrains have added

hydrogen to their aromatic rings, giving cyclohexane or cyclohexene structures; in these vitrains, however, part of the lithium is consumed by attack on oxygen functions and by reaction with the solvent. Vitrains of higher rank also add hydrogen to aromatic structures; since they have more aromatic structures and fewer oxygenated groups, they offer more opportunity for addition of hydrogen. With the very highest rank vitrains, the insolubility of the material tends to overcome the large number of reducible structures, so that the hydrogen uptake decreases. The maximum in the curve is therefore quite reasonable. Further experiments with other vitrains will define the curve more clearly. It should be pointed out that since coal is not a pure compound, two vitrains of the same carbon content may have quite different structures; hence, a certain scatter in the experimental points is to be expected.

Given, Lupton, and Peover⁴ have recently reduced a series of whole coals with lithium-ethylamine. The report of their work is quite brief, and exact experimental details are not known. Without further details, it is not possible to put the results of Given and the present results on a strictly comparable basis. However, it appears that lithium-ethylenediamine is more effective than lithium-ethylamine, especially for high rank materials.

Van Krevelen⁵ has given a comprehensive discussion of the value of the atomic H/C versus O/C diagram, both in the study of coals and in the study of the changes which take place in coals upon chemical treatment. In most of the vitrain reductions reported here, the analytical results indicate that the reduced sample is higher in both hydrogen and oxygen than is the starting material; reduction has increased the numerical values of both the H/C and O/C ratios. Such a change can best be explained by a combination of hydrogenation and hydration. The exact pathway by which hydrogen is added is not certain;² presumably lithium atoms add to the unsaturated structures, and are then replaced by hydrogen atoms, which probably come from the amino groups of ethylenediamine.

In figure 2, each of the vitrains reduced is plotted on the H/C versus O/C diagram. They show the changes which can be attributed to hydrogenation and dehydration, as discussed above.

We have determined pyridine solubility at room temperature for six of the reduced vitrains. Figure 3 and Table IV show the solubilities of the starting and reduced materials. Vitrains in the 82-85 percent carbon range are moderately soluble; reduction causes a moderate increase in solubility. Probably this is due largely to the addition of hydrogen to aromatic rings, since hydroaromatic structures are generally more soluble than the corresponding aromatic molecules. Vitrains in the range of 89-90 percent carbon are of very limited pyridine solubility, because the molecules are fairly large and contain a number of aromatic rings; on reduction, considerable conversion to hydroaromatic structures takes place with a great increase in solubility. A 91 percent carbon vitrain is insoluble both before and after reduction. Here, the platelet size has increased to such a degree that even the highly reduced hydroaromatic types of structures are too large to be soluble.

A typical infrared spectrum is shown in figure 4. The reduced materials show increased C-H absorption at 3.5μ , decreased absorption at 6.2μ , and decreased absorption in the three bands at 11.5 , 12.3 , and 13.3μ .

The ultraviolet spectra of the reduced materials show decreased absorption. Table V shows the change in extinction coefficient (K) for four of the vitrains; although the data are only semiquantitative, the large changes in K, particularly

for the Pocahontas vitrain, indicate a decrease in aromatic structures. Electron paramagnetic resonance measurements show that reduction causes a marked decrease in the number of free radicals. Table VI shows the change in free radical content of the vitrains after reduction. This data is consistent with a large decrease in aromatic structures.

Examination of scattered X-ray intensities of the reduced vitrains^{6/} revealed that extensive changes had occurred in the arrangement of carbon atoms. The most apparent major change was in the (002) reflections, the most prominent part of the vitrain patterns. At first glance at the intensity curves, one might presume that a new band has appeared in the angular range corresponding to spacings of 4 to 5 Å, in place of the (002) band at 3.6 Å. This change in the intensity patterns as a result of reduction can be considered mainly a displacement of the (002) band assuming that carbon atoms in the hydrogenated layers are now slightly displaced from planar positions forming buckled layers.

A striking result of the lithium reduction of vitrains is the great reduction in sulfur content, as can be seen from Table II. It is possible that this may be of value in desulfurizing coals on a large scale. Some indication of the way in which sulfur is eliminated was obtained by treating dibenzothiophene with lithium-ethylene-diamine; the products are shown in Figure 6. It appears likely that the first attack on dibenzothiophene results in the splitting of a carbon-sulfur bond to give a substituted thiophenol; the unsubstituted ring is then reduced. As with phenols, the sulphydryl group protects the ring to which it is attached.

In order to determine whether the lithium reduction proceeds to completion under our arbitrary conditions, a large batch of Bruceton vitrain was reduced. Some of this material was then reduced a second time and then a third time. Table VII gives the analytical data for these samples. It can be seen that the reduction on a large scale did not give as large a hydrogen pickup as the small scale reductions, and that the second and third reductions give little or no additional hydrogen uptake. The infrared spectra also showed essentially no changes. The X-ray diffraction patterns, however, did show that the second and third reductions caused further alteration in the vitrain structure. The nature of these changes is not known at the present time.

The reduced Bruceton vitrain was submitted to the Fischer-Schrader low temperature carbonization assay. The results are given in Table VIII. It can be seen that the reduced material forms less coke and more tar than does the starting vitrain. This is probably a reflection of the higher hydrogen content of the reduced vitrain. Table VIII also gives the ASTM free swelling index, and the composition of the coke formed.

Using 3 gram samples, the largest amount of reduction was achieved with the Pocahontas vitrain (44 atoms of hydrogen per 100 carbon atoms in the starting material - see Table III). We have observed that scaling down of the reaction results in greater reduction of the vitrain. Thus, when a one gram sample of Pocahontas vitrain was reduced (one third of the amounts of lithium and ethylenediamine used), 56 atoms of hydrogen were added per 100 carbon atoms in the starting vitrain. One may conclude that over half the carbon atoms in this particular vitrain are involved in carbon-carbon double bonds.

Experimental Procedures

a. Reductions

All operations described below were conducted under nitrogen in a dry box, or were rapidly performed with minimum exposure to air. In general, all grinding, crushing, and screening operations were performed in the dry box. Vitrains were crushed to -6 mesh and stored under nitrogen. Portions of approximately 8 grams were removed and ground to -60 mesh in a mortar and pestle. Grinding was continued overnight in a small ball mill (sometimes a steel mill, but usually a small borundum mill). The ball mill and its contents were given a brief drying (60° and 1 mm. for 1-2 hours) to facilitate screening through a 325 mesh sieve. Approximately 6 grams of -325 mesh material was dried to constant weight at 60° and 1 mm. All dryings in the vacuum oven were terminated by admitting nitrogen and quickly closing the containers as soon as the oven door was opened.

The apparatus consisted of a 500 ml. 3-neck flask with two vertical necks and one side-neck at an angle of 20°. A thermometer was inserted through the 20° angle neck. The center neck was fitted with a mercury-sealed double Hershberg tantalum wire stirrer. The third neck carried an adapter with two condensers, a short stoppered one through which the lithium was added, and a larger spiral condenser, with a mercury-sealed gas inlet tube. Three grams of vitrain prepared as above was quickly weighed in a weighing bottle. The apparatus was flushed with prepurified nitrogen (prepurified nitrogen was used throughout, except for the oxygen-free water dispenser, where ordinary nitrogen (0.2 percent oxygen) was used). Fifty ml. of ethylenediamine was added and the stirrer started. The vitrain was then added, followed by 100 ml. of ethylenediamine. This procedure insured complete dispersion of the vitrain and precluded formation of lumps of agglomerated material. The temperature was raised to 90° and addition of lithium begun. A total of 6.8 grams of lithium was added in the course of 3 hours while the temperature was maintained at 90-100°. Stirring was continued for 1 hour at 90-100°. The reaction mixture was then cooled in an ice bath and approximately 250 ml. of water was added with vigorous stirring. (All water used was boiled and then stored and dispensed under nitrogen.) The mixture was then diluted to approximately 3200 ml. and transferred to 235 ml. polyethylene bottles, centrifuged for 15 minutes at 2500 r.p.m. and 25° and allowed to stand overnight. The clear supernatant solution was decanted and discarded. The residue was transferred to a 1 liter erlenmeyer flask and heated on a wax bath at 125-135° in a stream of nitrogen to dryness. Drying was continued in a vacuum oven at 60° and 1 mm. This operation, by removing ethylenediamine and agglomerating the vitrain, facilitates the final washing with water. The dried residue was ground to -40 mesh and transferred to polyethylene centrifuge bottles. Repeated washing and centrifugation were continued until the washings had a pH of 8 (test paper). This required 7-10 centrifugations. The alkali-free residue was transferred to a 250 ml. erlenmeyer flask and dried in a wax bath at 125° in a stream of nitrogen. Drying was continued in a vacuum oven. The sample was then ground (small stainless steel mill) and screened to pass 325 mesh. It was then dried to constant weight at 60° and 1 mm. For analysis, the starting vitrain was dried again at the same time.

It should be noted that duplicate experiments checked quite closely.

Recoveries were much better than is indicated by the percent recovery figures in Table II. Manipulations in the dry box result in considerable loss. Presumably the recovery might be based on recovery in the 250 ml. erlenmeyer flask, since the

final removal from the flask, grinding, and sieving account for considerable loss. However, the weight in the 250 ml. flask is not recorded since complete dryness is not possible with a sample of large particle size.

b. Solubility Determinations

All samples were redried for 1 hour at 60° and 1 mm. One hundred mg. samples were weighed and transferred to 45 ml. glass-stoppered test tubes with the aid of 15 ml. of dry pyridine. The stoppers were fastened in place with rubber bands, and the test tubes were shaken on a mechanical shaker for 1 hour. The mixtures were then filtered onto 15 ml. fritted-glass filter crucibles (medium porosity). The residues were washed 3 times with 5 ml. portions of pyridine. This was found sufficient to insure that the last washing was colorless. The crucibles were dried to constant weight (95° and 1 mm.). This required 1 to 3 hours. The percent solubility reported was obtained by subtracting the weight percent of residue from 100.

c. Large scale reduction of Bruceton vitrain

Approximately 400 grams of Bruceton vitrain were ground to pass through 325 mesh and then dried at 60° and 1 mm. Four portions of the above material were reduced by lithium in ethylenediamine.

Vitrain (68 grams) was added to 3400 ml. of ethylenediamine in a 5-liter flask. The resulting slurry was stirred and heated to 90-100° before gradual addition of a total of 153 grams of lithium wire. The addition of lithium required 12 hours. The rate of addition was determined by hydrogen evolution as observed in a mercury bubbler. After addition of lithium, the mixture was stirred and heated at 90-100° for another hour. The reaction mixture was cooled in ice water and decomposed by the addition of one liter of water. This slurry was then diluted to a final volume of approximately 18 liters. The slurry was allowed to stand from one to four days; during this time the clear supernatant liquid was decanted and discarded. The residue was then centrifuged at 2700 r.p.m. in 250 ml. polyethylene bottles. The clear supernatant liquid was again decanted and discarded. The residue was transferred to a 1.5-liter erlenmeyer flask which was heated to 125-135° in a wax bath while a current of nitrogen was passed in; this treatment was continued until the product was almost dry. The drying was continued at 60° and 1 mm. in a vacuum oven. This drying operation was intended to agglomerate the recovered anthraxylon and facilitate further washing and removal of lithium salts. The dried residue was ground to pass through 40 mesh and then washed with water and centrifuged repeatedly until the washings were almost colorless and the pH was about 9. This required about ten washings. The residue was again freed of most of the moisture by heating to 125-135° in a stream of nitrogen. The product was ground to pass 100 mesh and drying was then completed at 60° and 1 mm.

Four batches of anthraxylon were reduced in this manner. The percentage recovered in each of the four batches was 89.2, 81.1, 85.1, and 77.8 percent.

It should be noted that the procedure for the last batch differed slightly in that lithium was added to the reaction mixture maintained at 95-105° instead of the usual 90-100°.

The products were submitted for infrared analysis by the potassium bromide pellet technique. The spectra of the four batches were sufficiently similar to each other and to previous reductions of Bruceton anthraxylon to justify mixing them to

make one large sample. The batches were combined, ground to pass 325 mesh, and again dried at 60° and 1 ml. A total of 228 grams of reduced Bruceton anthraxylon was produced.

The material described above is called the first reduction in Table VII. Twelve grams of this material was reduced again in a similar manner; this is the second reduction in Table VII, 8.33 g. being recovered. For the third reduction, 8.04 g. was reduced, 6.11 g. being recovered.

This work was carried out as part of a cooperative agreement between the Bureau of Mines and the Union Carbide Corporation.

Acknowledgments

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References

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- 2/ L. Reggel, R.A. Friedel, and I. Wender, *J. Org. Chem.* 22, 891 (1957).
- 3/ L. Reggel, R. Raymond, and I. Wender, unpublished work.
- 4/ P.H. Given, V. Lupton, and M.E. Peover, Preprints of Meeting "Science in the Use of Coal," University of Sheffield, April 1958; *Nature* 181, 1059 (1958).
- 5/ D.W. van Krevelen, *Fuel* 29, 269 (1950).
- 6/ S. Ergun and I. Wender, *Fuel* 37, 503 (1958).

Table I.- Vitrain samples used in 3-gram runs

Run No.	
7R-80	Rock Springs Nos. 7, 7½, 9, and 15 coal beds, Superior, Sweetwater County, Wyoming.
7R-76	Bruceton, Pittsburgh Bed, Allegheny County, Penna.
7R-69	Pond Creek Bed, Majestic Mines, Pike County, Kentucky.
7R-73	Powellton Bed, Elk Creek No. 1 Mine, Logan County, W. Va.
7R-71	Sewell Bed, Marianna Mine, Wyoming County, W. Va.
7R-75	Pocahontas No. 3 Bed, Stephenson, Wyoming County, W. Va.
7R-72	Anthracite, Dorrance Mine, Lehigh Valley Coal Company, Luzerne County, Penna.
7R-79	Madagascar flaky graphite.

Table II.- Microanalysis of vitrains before and after reduction
(dried at 60°C and 1 millimeter)

Name	Number*	Carbon	Hydrogen	Nitrogen	Sulfur	Ash	Oxygen (diff.)	Percent recovery
Rock Springs	80	76.25	5.76	2.04	0.87	0.86	14.22	
	80A	72.78	7.21	5.20	0.33	2.00	12.48	40.3
Bruceton	76	80.65	5.42	0.96	1.13	2.27	9.57	
	76A	75.73	6.93	3.81	0.29	2.82	10.42	69.9
Pond Creek	69	82.63	5.15	1.15	0.69	2.25	8.13	
	69A	77.35	7.24	3.05	0.23	2.19	9.94	61.5
Powellton	73	83.63	5.00	1.59	0.46	1.52	7.80	
	73A	79.15	6.58	2.95	0.15	1.94	9.23	76.1
Sewell	71	87.29	5.03	0.97	0.63	2.31	3.77	
	71A	81.42	7.33	2.34	0.19	2.66	6.06	64.3
Pocahontas	75	87.66	4.35	1.49	0.58	2.42	3.50	
	75A	82.04	7.46	2.09	0.12	3.65	4.64	85.5
Anthracite	72	89.02	2.55	1.08	0.60	2.31	4.44	
	72A	81.70	4.93	1.91	0.07	1.96	9.43	71.7
Graphite	79	98.93	0.24	0.18	0.00	0.00	0.65	
	79A	85.76	2.96	3.92	0.00	0.00	7.36	104.0

* A indicates reduced material.

Table III.- Microanalyses of vitrains before and after reduction
(Moisture, ash, sulfur, and ethylenediamine-free basis)

Name	No. *	Carbon	Hydrogen	Nitrogen	Oxygen (diff.)	Grams hydrogen added per 100 g. starting MASF vitrain	Grams water added per 100 g. starting MASF vitrain	Atoms hydrogen added per 100 carbon atoms	Molecules water added per 100 carbon atoms
Rock Springs	80	77.58	5.86	2.08	14.48				
	80A	77.22	6.91	(2.08)	13.79	1.16	-0.69	17.7	-0.6
Bruceton	76	83.46	5.61	1.81	9.12				
	76A	80.05	6.84	(1.81)	11.30	1.18	3.08	16.9	2.5
Pond Creek	69	85.12	5.30	1.18	8.40				
	69A	81.00	7.07	(1.18)	10.75	1.75	3.33	24.5	2.6
Powellton	73	85.32	5.10	1.61	7.97				
	73A	82.13	6.50	(1.61)	9.75	1.37	2.51	19.2	2.0
Sewell	71	89.94	5.18	1.00	3.88				
	71A	85.20	7.35	(1.00)	6.46	2.20	3.36	29.1	2.5
Pocahontas	75	90.37	4.47	1.54	3.62				
	75A	85.89	7.67	(1.54)	4.90	3.40	1.82	44.8	1.3
Anthracite	72	91.68	2.62	1.11	4.59				
	72A	84.21	4.87	(1.11)	9.81	1.90	6.97	24.7	5.1
Graphite	79	98.93	0.24	0.18	0.65				
	79A	89.77	2.04	(0.18)	8.01	0.98	9.22	11.8	6.2

* A indicates reduced material.

Table IV.- Solubility of reduced anthraxylons in pyridine
at room temperature

	% C (maf)	% Soluble, untreated	% Soluble, reduced	% Increase in solubility
Bruceton	82.50	21.4	30.7	43
Pond Creek	84.53	13.2	38.1	113
Powellton	84.88	20.9	36.6	75
Sewell	89.38	2.5	90.9	3636
Pocahontas	89.85	3.9	62.5	1502
Anthracite	91.16	0	0	0

Table V.- Ultraviolet absorption of vitrains

Name	No.	% C	Specific extinction coefficient K (liters/g. gm.) at 4000 A		$\frac{K \text{ reduced}}{K \text{ original}}$
			original	reduced	
Bruceton	76A	82.50	10.1	8.0	79
Powellton	73A	84.88	12.9	5.3	41
Sewell	71A	89.38	13.5	6.8	50
Pocahontas	75A	89.85	26.9	4.6	17

Table VI.- Free radical content of vitrains

Name	No.	% C	Free radical concentration (arbitrary units)	
			original	reduced
Harmatten	70A	77.20	112600	54500
Bruceton	76A	82.50	207000	89300
Powellton	73A	84.88	270000	77200
Sewell	71A	89.38	635000	72000
Anthracite	72A	91.16	2400000	2186000

Table VII.- Repeated reduction of Bruceton vitrain

Run No.	Treatment	C H N S				O (diff.)	Li
		(Ash and ethylenediamine- free basis)					
7R-60	Starting material	81.52	5.32	1.13	1.05	10.99	trace
7R-60F	First reduction	79.08	6.03	(1.13)	0.30	13.46	0.30
7R-65	Second reduction	75.14	6.09	(1.13)	0.08	17.56	-
7R-67	Third reduction	79.60	5.92	(1.13)	0.05	13.30	0.23

Table VIII.- Fischer-Schrader low temperature carbonization assay
(500° C.) and ASTM free-swelling index (823° C.)

	Bruceton vitrain 7R-60	Reduced Bruceton vitrain 7R-60-F
Coke	78.3	63.5
Tar	10.9	22.2
Water	6.8	9.4
Light oil	0.51	0.77
Gas	3.5	4.1
F.S.I.	7½	5½
Coke, percent	70.2	52.4
Composition of coke		
C	84.54	83.35
H	3.64	3.64
N	1.81	3.77
S	0.83	0.21
Ash	2.69	3.87

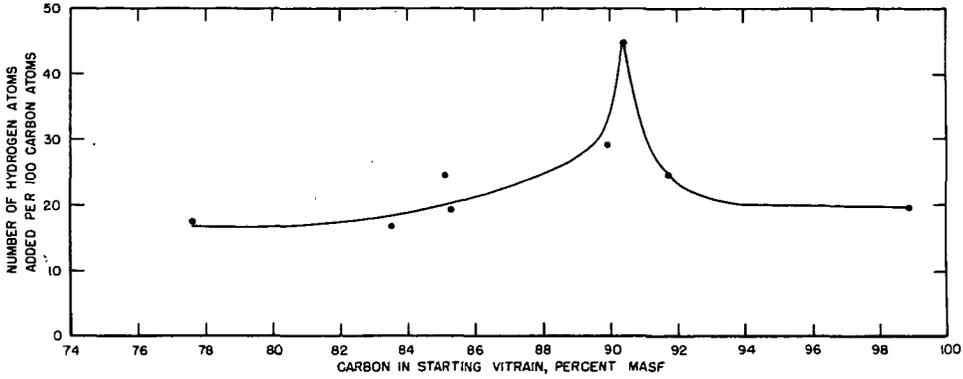


Figure 1 - Hydrogen uptake of vitrains.

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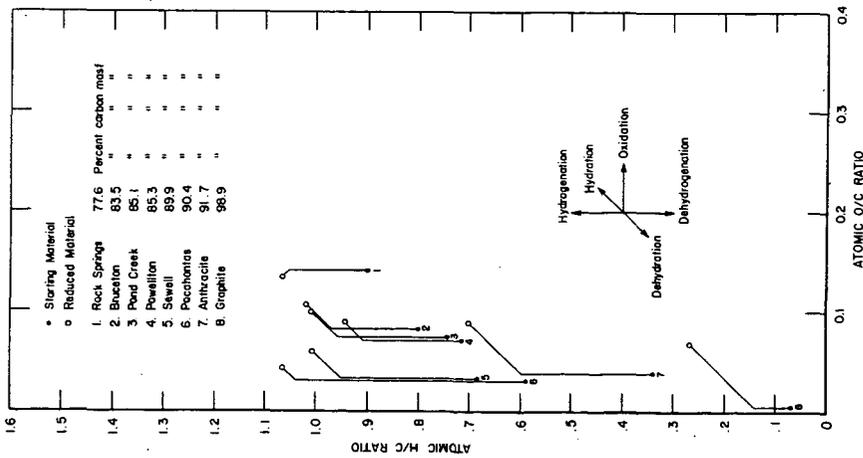


Figure 2 - H/C vs. O/C diagram for vitrains.

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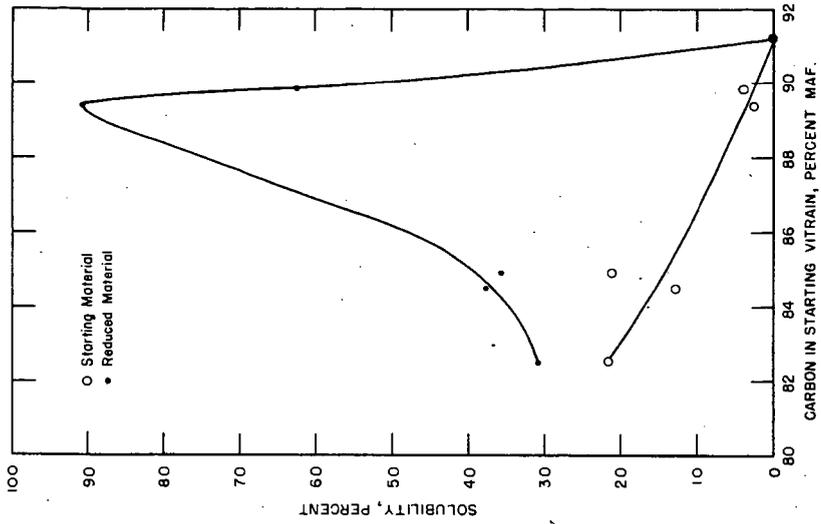


Figure 3 - Solubility of vitrains in pyridine at room temperature.

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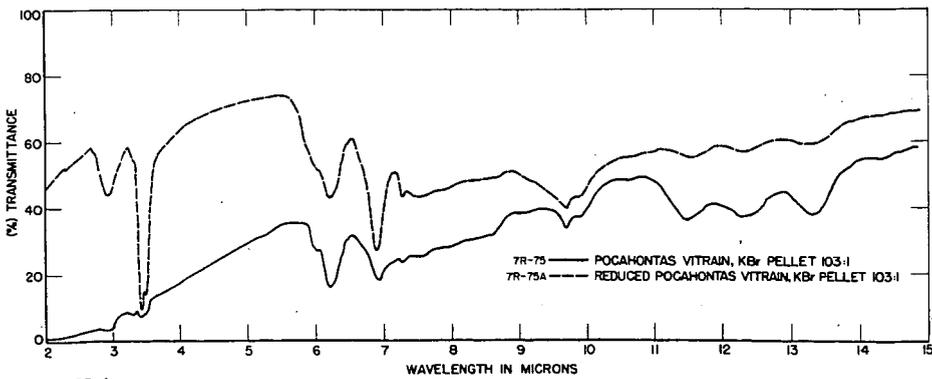


FIGURE 4.

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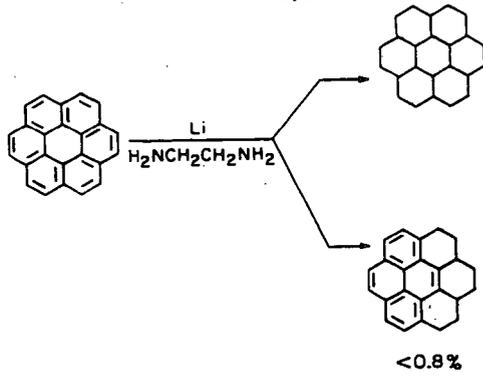


FIGURE 5.-- REDUCTION OF CORONENE

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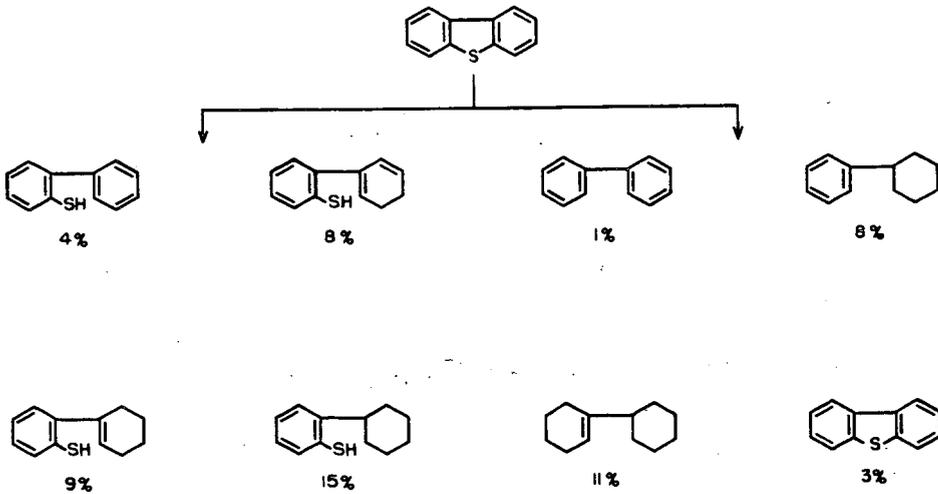


FIGURE 6.

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