

COMMUNICATIONS TO THE EDITOR

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THE POLAROGRAPHIC REDUCTION OF ARYL SELENOXIDES

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Though the polarographic reduction of aryl sulphoxides^{1,2} has been reported, the behaviour of selenoxides at the dropping mercury electrode (D.M.E.) has not been previously investigated. We have found that dibenzyl and diphenyl selenoxides are reduced in what is probably a two-electron process and propose that the mechanism involves reduction to selenide.

A Tinsley pen-recording polarograph, with thermostated H-cell, was used to obtain the polarograms. A mixed solvent consisting of benzene (10%, v/v), water (20%), and methanol (70%) was used with tetramethylammonium bromide as base electrolyte. The selenoxides were prepared by oxidation of the selenides with hydrogen peroxide.³

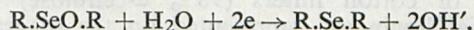
Diphenyl and dibenzyl selenoxides give well-defined waves, the heights of which vary linearly with concentration up to $10^{-3}M$; above this concentration maxima are observed. The half-wave potential of diphenyl selenoxide is less negative than that of diphenyl sulphoxide,² which is consistent with the greater ease of chemical reduction of selenoxides. The electrode process is diffusion controlled, as the current varies linearly with the square root of the applied mercury pressure. Thus, using the Ilkovic equation and the polarographic diffusion coefficient of a suitable reference compound, the number of electrons involved in the electrode process can be calculated. Benzophenone is a molecule with a similar reduction potential which, from the rather naïve consideration of molecular dimensions, would be expected to have a similar rate of diffusion to that of the selenoxides.

Table

Substance	Half-wave Potential versus S.C.E.	Diffusion Current Constant. For the Capillary used, $m^{2/3}t = 1.612$	Number of Electrons Involved
Diphenyl selenoxide	-1.43 volts	4.28	1.75
Dibenzyl selenoxide	-1.28 "	3.80	1.55
Benzophenone	-1.40 "	4.90	2.7

Generally, the products of polarographic and chemical reductions are similar. As selenoxides are

reduced to selenides by various agents,⁴⁻⁶ and as selenides do not give waves at the D.M.E., it is not unreasonable to suggest the following two-electron reduction process at the electrode surface:



That the calculated values of the number of electrons involved are less than two may be ascribed to the high degree of solvation of the selenoxide molecules, which results in a lower diffusion coefficient than for benzophenone.

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INFRARED ABSORPTION SPECTRA OF PRODUCTS OF CARBONISATION OF CELLULOSE AND LIGNIN

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Numerous experiments have been carried out on the carbonisation of cellulose, lignin and other constituents of wood.¹ Also various theories have been advanced on the origin of coal, such as the "cellulose" theory of Bergius and the "lignin" theory of Fischer and Schrader.²

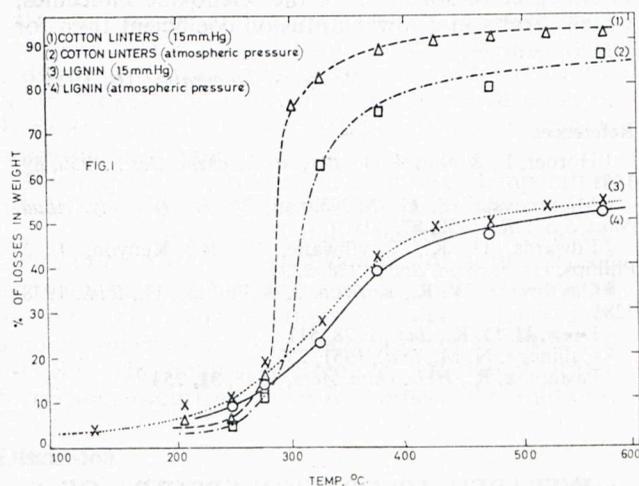
In this Communication we describe our experiments on the infrared absorption spectra of the products of thermal decomposition of cellulose and lignin.

Samples of cellulose and lignin (4 g. and 3 g. respectively) were inserted in a glass tube of 26 mm. diameter, heated in an electric furnace to a definite temperature with deviations $\pm 2^\circ C$. obtained by automatic regulation. Nitrogen was slowly drawn through the tube, in order to avoid decomposition of the samples by oxygen of the air and to remove the volatile decomposition products. Inside the

tube either atmospheric or 15 mm. Hg pressure was maintained by means of a water pump. Heating of the samples was continued until no further decomposition could be detected, i.e. no more gaseous products were evolved and the constant weight of the samples was attained: 2 hours were sufficient to obtain this state.

After that, all samples were subjected to elementary analysis and to examination of their infrared absorption spectra in Nujol mull (ratio 50:50) for the range 4500 to 750 cm^{-1} . A Hilger 800 double-beam spectrophotometer with sodium chloride prism was used.

The results of analysis of the decomposition products of cotton linters (98% α -cellulose) and commercial lignin are represented on the diagrams (Figs. 1 and 2).



There is a considerable increase in losses of the weight of cellulose and lignin near 300° and 350°C. respectively in both types of decomposition, under reduced and atmospheric pressure.

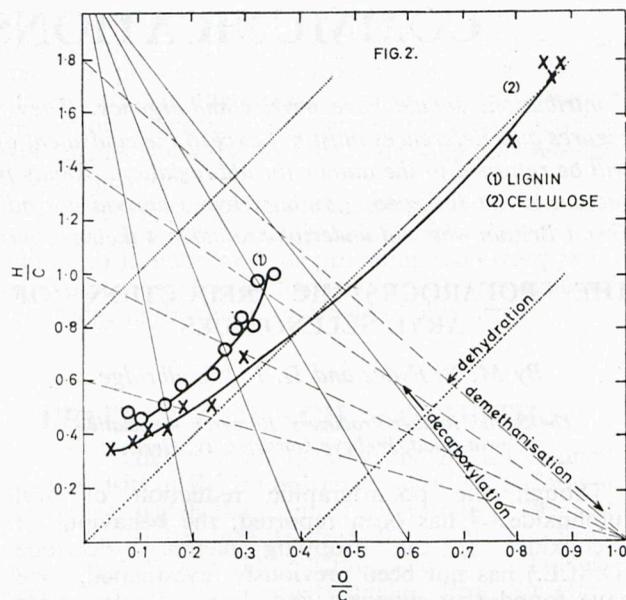
The figures for wood cellulose (96% α -cellulose) do not differ essentially from those for the cotton linters.

A sharp fall of the atomic ratios H:C and O:C (particularly in the case of cellulose) is also seen on the van Krevelen diagram (Fig. 2).

Typical absorption spectra are given in Figs. 3 and 4. They are related to decomposition under reduced pressure of cotton linters and lignin respectively. The ordinates of the absorption curves are shifted to higher values with the increase of the carbonisation temperatures, to have a clearer presentation of their shapes.

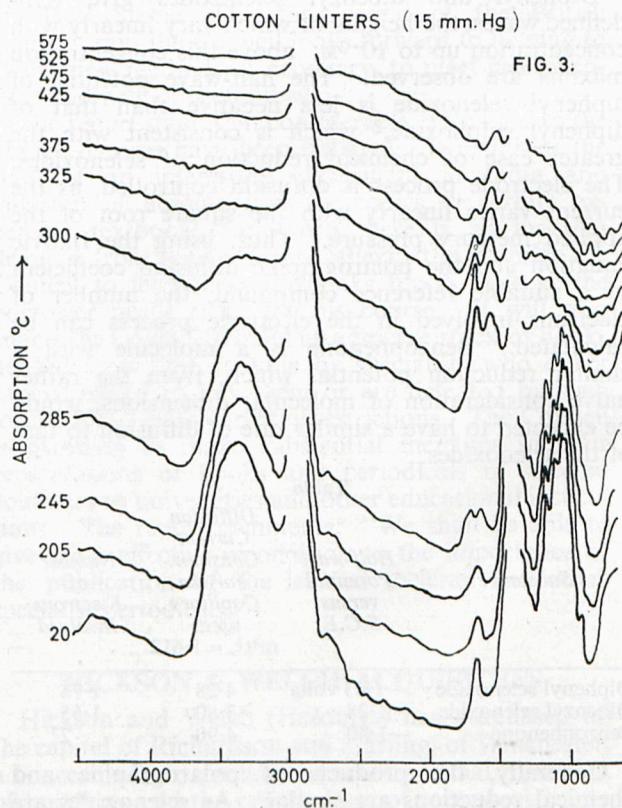
Cellulose.—There is a clear cut between the shape of the absorption spectra of carbonisation products decomposed below and above 300°C.

Hydrogen-bonded hydroxyl group vibration modes (3300 cm^{-1}) weaken with the increase of temperature and disappear above 370°C. A band at 1640 cm^{-1} weakens with temperature and disappears above 245°C. This band is most likely due to water present



in cellulose, as we found a strong band of the same frequency in sugar hydrates.³

The samples decomposed at 300°C. and above show a frequency 1690–1695 cm^{-1} , probably of the aromatic carbonyl group. Another frequency (1595–1600 cm^{-1}) shift at higher temperature of carbonisation towards lower frequencies (1570 cm^{-1}) should probably be ascribed to aromatic skeletal vibrations.



Three frequencies, 1155 cm^{-1} , 1105 cm^{-1} , and 1025 cm^{-1} , should probably be ascribed to acetal bonds in cellulose. All of them disappear at temperatures near 525°, 370° and 420°C. respectively. The 1050 cm^{-1} frequency of the C-O bond joining carbon and a hydroxyl group weakens above 245°C. and disappears above 370°C.

At higher temperatures (425° and 475°C.) new aromatic frequencies (870 and 800 cm^{-1} respectively) appear (C-H out of plane deformations in highly condensed aromatic systems⁴).

Undoubtedly aliphatic structure begins rapidly to disappear above 300°C. and is gradually replaced by an aromatic condensed system. The pattern of the absorption curve of the highly carbonised samples (at 525–575°C.) is much the same as that of anthracite and graphite.

Lignin.—A similar change is produced with lignin, although it is much less pronounced, as the starting substance has essentially an aromatic structure.

Typical hydrogen-bonded hydroxyl bands (frequency 3200–3300 cm^{-1}), phenolic C-O (frequency 1265 cm^{-1}), and C-O frequency of alcohol and ether groups (1140, 1075 and 1030 cm^{-1}) are gradually weakening with increasing temperature and eventually disappear at 275°, 520°, 375°, 375°, 375°C. respectively. Also that due to the C-O band (1695 cm^{-1}) disappears at 375°.

A few aromatic frequencies such as 1570 cm^{-1} . (=C skeletal in-plane vibrations), 860, 810 cm^{-1}

(both of C-H out of plane deformation) exist throughout all samples. The band 1175 cm^{-1} (substituted aromatic ring) disappears at 575°C. probably as a result of the formation of a condensed aromatic system.

Here also the absorption curves of samples of the highest degree of carbonisation resemble very much those of anthracite and graphite.

It is proposed to publish elsewhere⁵ a more detailed paper.

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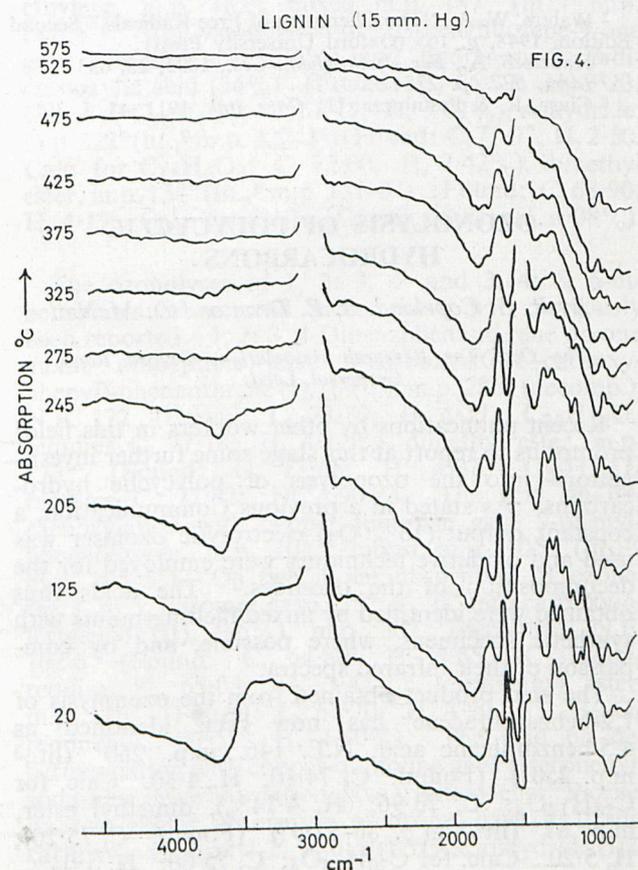
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FORMATION AND STABILITY OF ARYLDIAZONIUM IODIDES AND TRI-IODIDES

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The formation in some cases of an isolable aryldiazonium tri-iodide when a solution of the aryldiazonium sulphate in excess of acid is mixed with aqueous alkali iodide has recently been demonstrated, and it has been shown that these tri-iodides decompose on warming to give the aryl iodide, nitrogen, and iodine.¹ These results support an earlier suggestion² that the effective anion in the replacement of the diazonium group by iodine in aqueous acid solutions is tri-iodide, and that its action is autocatalytic.

We have now isolated aryldiazonium tri-iodides, formed as above, in certain other cases. The following red-brown or maroon compounds were prepared as described previously,¹ by diazotising the amine in aqueous sulphuric acid with a slight excess of nitrite, and mixing with excess of aqueous potassium iodide at -5°: *o,p*-xylene diazonium tri-iodide, decomposing at 60° (Found: I, 69.3. C₈H₉N₂I₃·2H₂O requires I, 69.2%); *p*-methoxybenzene diazonium tri-iodide, decomp. 52° (Found: I, 68.5. C₇H₇ON₂I₃·2H₂O requires I, 68.8%); *o*-methoxybenzene diazonium tri-iodide, decomp. 38° (Found: I, 68.6%); *p*-chlorobenzene diazonium tri-iodide, decomp. 38°, *p*-toluene-diazonium tri-iodide, decomp. 30°, and benzene diazonium tri-iodide, decomp. 29°, were isolated but not analysed. The above-named compounds are all liable to decompose explosively when dry; since they cannot be recrystallised and decompose on standing, analytical values can only be regarded as