EPR IN CARBONIZED SACCHARIDES

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The dependence of the EPR spectra on the temperature of carbonization T_c was examined in carbonized samples of mono-, oligo- and polysaccharides. In all samples a simple line was found of Lorentzian line-shape with $g \doteq 2.0030 \pm 0.0010$. The line-widths are changing in an interval from 5.0 to 9.0 Oe depending on the origin of the sample. The spin concentration depends on the origin of the sample and passes through a flat maximum depending on T_c.

I. INTRODUCTION

Measurements of the EPR spectra in products of the carbonization of different materials of organic origin are made for explaining the formation of paramagnetism in these materials and elucidating the course of their thermal decomposition. Especially the violent increase of the intensity of EPR was noticed in combustion products with a percentual content of carbon $C \in \langle 80\%,\ 94\%\rangle$); the influence of the temperature of carbonization [2], [3] (the maximum of concentration of paramagnetic centre for temperatures $T_c \in \langle 500\ °C,\ 600\ °C\rangle$); further the influence of oxygen and of chemical treatment [2] on the EPR spectra. Generally a symmetrical singlet of a predominantly Lorentzian line-shape was observed in products of carbonization. The line width was observed [3] for various materials from 1 to 100 Oe, the g-factor approaches the g-factor of the free electron. The concentration of paramagnetic centres in some carbonized materials reached as much as $\sim 10^{20}\ g^{-1}$ [4]. Analogical EPR effects were observed in natural coals [5] and in ,,artificial coals", prepared by carbonization or irradiation (e.g. sugar, charcoal, carbon black, pitch [6, 7]). The explanation of the origin of paramagnetism in these substances led to the same results. Two kinds of unpaired electrons are created in carbonized organic materials according to [8]. They

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are movable π-electrons in low-temperature samples, which are stabilized on condensed aromatic rings by the resonance energy. Their concentration falls with the increase of T_c over 700 °C and decays completely at $T_c \doteq 1000$ °C and more. At temperatures greater than 1400 °C probably immobile σ-electrons are observed, produced from broken C—C bonds, localized on defects in the graphitized lattice. Some authors [6], however, refer to the possibility of paramagnetism in these substances without the formation of the usual free valences.

The present paper deals with EPR in organic materials, whose structure was artificially damaged by carbonization. The results about EPR spectra in carbonized saccharides published so far refer mostly to saccharose [3] and glucose [9, 18] only, without connexion to other saccharides. We investigated the EPR spectra of carbonized samples of mono-, oligo- and polysaccharides as components of a certain group of organic compounds-saccharides with respect to both their common and distinct properties. The following samples were prepared from:

a. monosaccharides: pentoses — D-ribose, D-xylose, D-lyxose, L-arabinose ($C_5H_{10}O_5$), hexoses — D-mannose, D-glucose, D-galactose, D-fructose, L-sorbose ($C_6H_{12}O_6$),

b. oligosaccharides: disaccharides ($C_{12}H_{22}O_{11}$) — trehalose, maltose, cellobiose, lactose, saccharose,

c. polysaccharides: cellulose, starch, glycogen.

II. EXPERIMENTAL PART

1. Preparation of the samples

The pyrolytic decomposition takes place upon heating the saccharides above their melting points; during this process water, CO_2, CO and a quantity of minor organic compounds are liberated. Besides the primary saccharides there are produced di-, trisaccharides and higher polymeric substances. The residue of the pyrolysis is probably a high polymer. Pure carbon is formed at a very high temperatures and after a long heating time.

The same products are produced upon the carbonization of samples both in an inert atmosphere and in vacuo [13—15]. During the carbonization of our samples there was a continuous draining of removal gaseous products. The investigated samples of saccharides were prepared as follows: Small quantities of saccharides in an anhydrous powdered state were placed into a quartz tube and put into a crucible furnace. A rotary oil pump was used

in a vacuum system. The condensable volatile substances were removed from the vacuum system by means of a cold trap so as not to contaminate the residue of the carbonization. In the cold trap a Dry Ice-acetone mixture (195 °K) was employed. The oven temperature was regulated with the aid of an autotransformer and checked with thermocouples with a measuring accuracy of ± 10 °C. The samples were carbonized in the temperature range of $T_c \in \langle 250 \text{ °C}, 750 \text{ °C}\rangle$. After the furnace had been heated quickly to the necessary temperature, it was maintained at a constant value for 30—45 minutes. The extension of the carbonization time has no substantial effect on the formation of the carbonized products [14]. The cooling of the samples to room temperature was also made in vacuo. The residues of the carbonized saccharides, prepared in this way, were pulverized and used in that form for measurements.

2. Measurements of the EPR spectra

The EPR spectra of the carbonized samples were measured at room temperature by the EPR spectrometer with a 100 kHz modulation in the 3 cm range [16]. The spectra of all the investigated samples are simple symmetrical lines. Such singlets are formed as a result of an absorption of energy at the reorientation of an isolated spin. The resonance condition is

$$hf = g\mu_B H,$$ (1)

where h — Planck's constant, f — the frequency of the microwave field, g — the spectroscopic splitting factor, μ_B — the Bohr magneton, H — the intensity of the constant magnetic field. For a complete description of these spectra there are determined the line-shapes, the line-widths, the g-factors and the concentrations of paramagnetic centres.

The line-shapes were determined by a direct comparison of the experimental spectra with the theoretical Lorentzian and Gaussian lines.

The line-width is given by:

$$\Delta H_{max} \doteq 2.3487 \times 10^{-4}(f_{max} - f_{min}) \qquad \text{[Oe, Hz]},$$ (2)

where the frequency difference of the extreme points of the absorption derivative line is measured by means of an NMR magnetometer.

The g-factor is obtained from Eq. (1):

$$g = \frac{hf}{\mu_B H_0},$$ (3)

where $H_0 \doteq 2.3487 \times 10^{-4} \times \frac{1}{2}(f_{max} + f_{min})$ [Oe, Hz].

The concentrations of paramagnetic centres in the examined samples were determined by the comparison of the EPR spectra in these materials with the standard EPR spectrum. Varian's „Strong Pitch" was used as the standard with a defined number of spins 3×10^{15} cm^{-1} of the effective length, with the Lorentzian line-shape. The spectra were compared under the same experimental conditions. The number of paramagnetic centres in the investigated samples is defined by [6]:

$$N_x = N_n \frac{(I_0' \Delta H^2_{max})_x}{(I_0' \Delta H^2_{max})_n},$$ (4)

where $(I_0')_x$; $(I_0')_n$ are the amplitudes of the absorption derivative lines of the sample and the standard, respectively. They are reduced due to the boundary effects of the resonator [15].

III. RESULTS AND DISCUSSION OF THE MEASUREMENTS

1. The line-shape

All the examined samples of the mono-, oligo- and polysaccharides had a line-shape of the Lorentzian type (with good approximation) in the whole
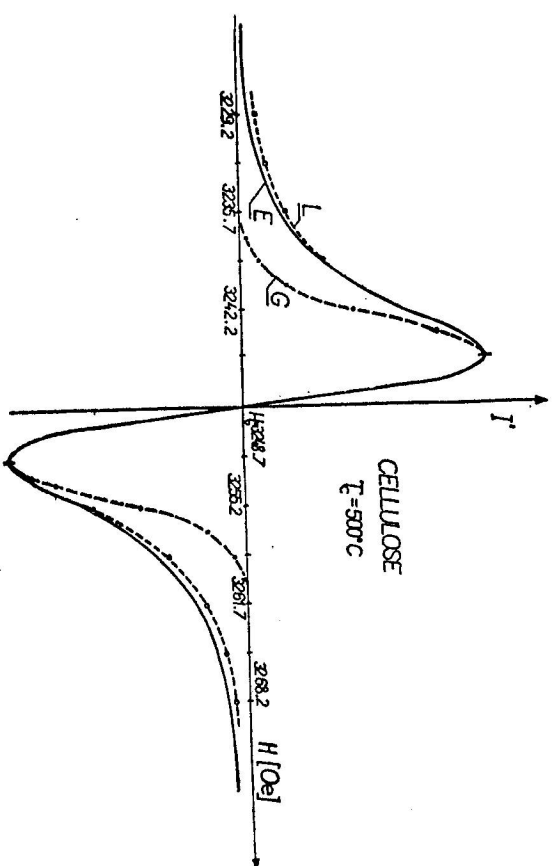

Fig. 1. The comparison of the first derivative absorption experimental curve of EPR with the theoretical curves with the same values of I_0' and ΔH_{max}. L-curve, G-the Gaussian curve, E-the experimental line for carbonized ce $\doteq 500$ °C).

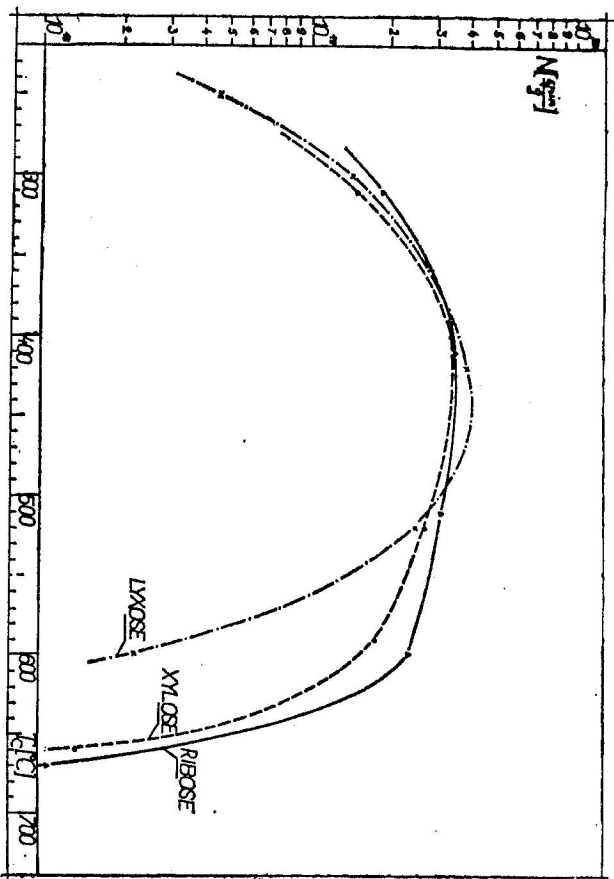interval of temperatures $T_c \in \langle 250 \,°C, 750 \,°C\rangle$. The characteristic record of the EPR spectrum in the tested samples is shown in Fig. 1, compared with the Lorentzian and Gaussian line-shapes. The changes of line-shapes with T_c were not observed in any series of carbonized samples.

Fig. 2. The dependence N [spin/g] on T_c [°C] for the carbonized p

2. The line-width ΔH_{max}

The line-widths are changed from 6.0 to 8.2 Oe for the carbonized monosaccharides, the pentoses have narrower lines than the hexoses. The line-widths of carbonized disaccharides are in the range from 5.0 to 6.7 Oe and of carbonized polysaccharides from 5.6 to 8.9 Oe. In general, the line-widths of the carbonized saccharides are between 5.0 and 9.0 Oe. No samples showed substantial and regular changes of $\Delta H_{max}(T_c)$.

3. g-factor

The calculated values of g-factors change in an interval of $g = 2.0030 \pm 0.0010$ for the various carbonized samples of saccharides. These values differ very
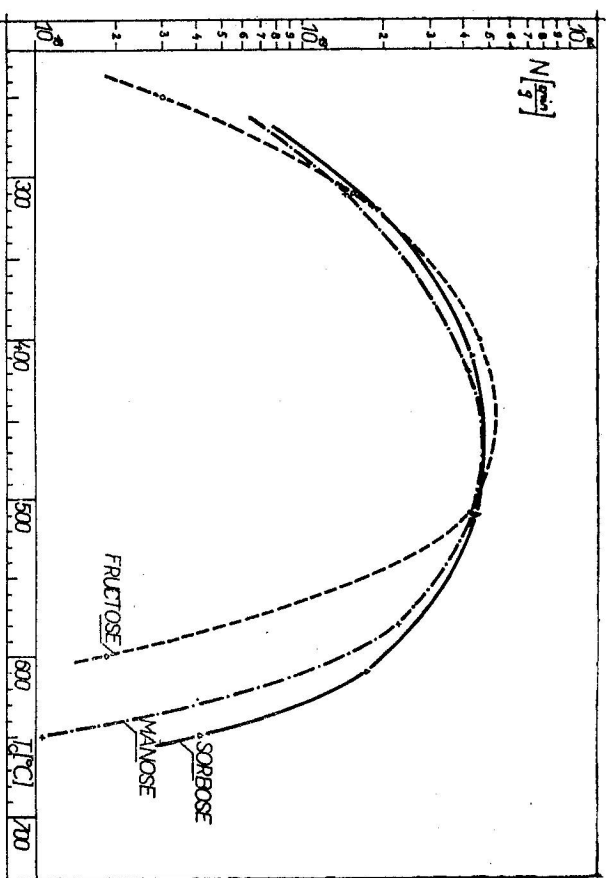
Fig. 3. The dependence N [spin/g] on T_c [°C] for the carbonized h

little from the g-factor of an isolated spin. They are constant in the temperature range of $T_c \in \langle 250 \,°C, 750 \,°C\rangle$ (within measurement errors) for all the series of the samples.

4. The concentration of paramagnetic centres

The main contribution of this paper is the observed dependence of the concentration of paramagnetic centres N in the carbonized samples of saccharides on the temperature of the carbonization T_c, (Figs. 2—5). For all samples an increase of N with T_c up to a certain maximum is observed, whose position is different for the individual series of the samples. The carbonized pentoses have the maximum of N at $T_c = 420 \,°C$, the hexoses at $T_c = 450 \,°C$.

The displacement of N_{max} to higher temperatures is more pronounced in the carbonized oligo- and polysaccharides; the maximum of N is at $T_c = 500 \,°C$ up to 520 °C. These phenomena may be explained with the aid of the analysis of the thermal stability of saccharides. The products formed from monosaccharides at lower T_c (~ 300 °C), are formed from oligo-
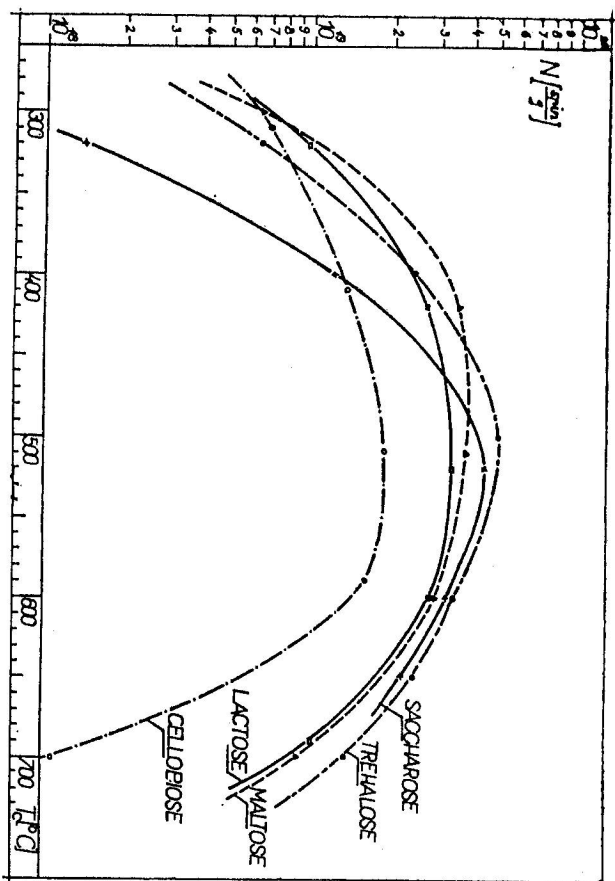
Fig. 4. The dependence N [spin/g] on T_c [°C] for the carbonized disa.

saccharides after the temperature T_c rises by ~ 50 °C. This follows also from the chemical analysis of the gaseous products of the pyrolysis.

All carbonized pentoses reach the maximum of concentration $N_{max} \doteq 3.5 \times 10^{19}$ spin/g, the hexoses up to 4.5×10^{19} spin/g. N_{max} is different for the various samples of carbonized di and polysaccharides from 1.9×10^{19} spin/g (cellobiose, cellulose) up to 5×10^{19} spin/g (trehalose). This fact, probably, depends on the structure of the molecule, i.e. on the monosaccharides it consists of, on how they are bound together and on the stability of these bonds. There is a remarkable agreement of N_{max} and of the whole course of $N(T_c)$ between cellulose and its derived oligosaccharid-cellobiose. Thus the concentration N does not increase proportionally to the polymerisation degree of the substance. The concentration N falls when the temperature T_c increases above the value, which determines the local maximum. The EPR signal decays at $T_c \doteq 600$ °C up to 650 °C for monosaccharides and at temperatures T_c over 700 °C, 750 °C for oligo- and polysaccharides.

Both the analogous course of dependence $N(T_c)$ and the order agreement in the concentration of paramagnetic centres (which are formed during the carbonization) for all series of saccharides indicate the same course of the thermal decomposition of mono-, oligo- and polysaccharides.
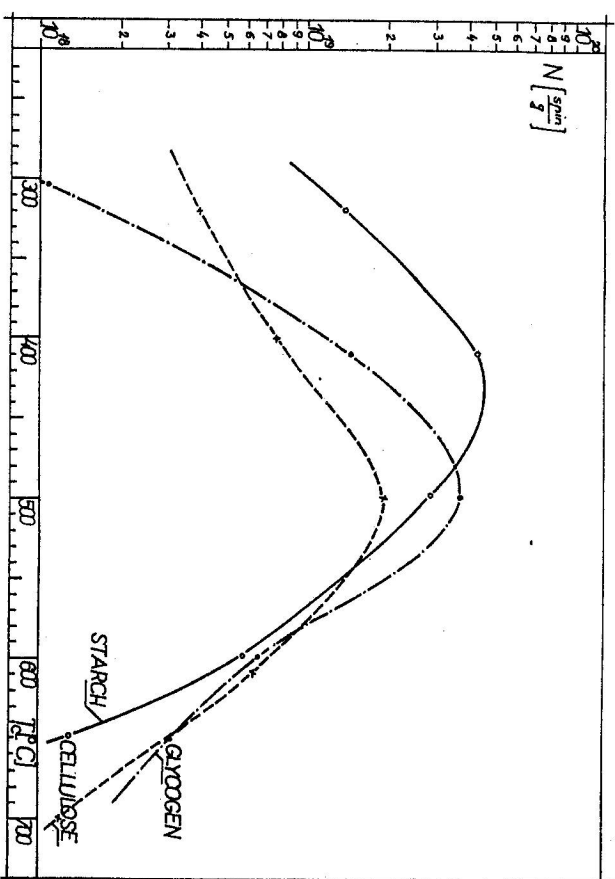
Fig. 5. The dependence N [spin/g] on T_c [°C] for the carbonized polysac.

5. Measurement in vacuo

A great group of coals of various origin [7] is known with a pronounced contact effect. During this investigation, the examined samples were pumped to a pressure of ~ 10^{-3} torr. They do not show the effects which could prove to the surface occlusion of the oxygen. This property is probably due to the preparation of the samples, because the carbonization of the saccharides and also their cooling were made in vacuo. Therefore, the adsorption of the oxygen could occur only after cooling to room temperature. The contact effect is probably caused by the chemisorption, which occurs during the carbonization in air.

IV. CONCLUSION

The singlet absorption spectrum of EPR was found in carbonized saccharides with the same EPR-properties as carbonized glucose [9], [15]. The samples of the carbonized saccharides may be used as EPR standards of spin-concentrations and g-factors. The use of these standards is convenient because of the thermal independence of their resonance properties. The standards are

easily prepared, they are stable and it is not necessary to store them in vacuo. It follows the results of this study that it is possible to employ as an EPR standard any carbonized saccharide from the investigated samples, which is pretreated at an optimum temperature (e.g. trehalose at $T_c = 520\ ^\circ C$).

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