FINSKA KEMISTSAMFUNDETS MEDDELANDEN

SUOMEN KEMISTISEURAN TIEDONANTOJA

REDAKTÖR — TOIMITTAJA
Tor-Magnus Enari

INNEHÅLL — SISÄLTÖ

N:o 4 • ÅRGÅNG 78 VUOSIK. • 1969

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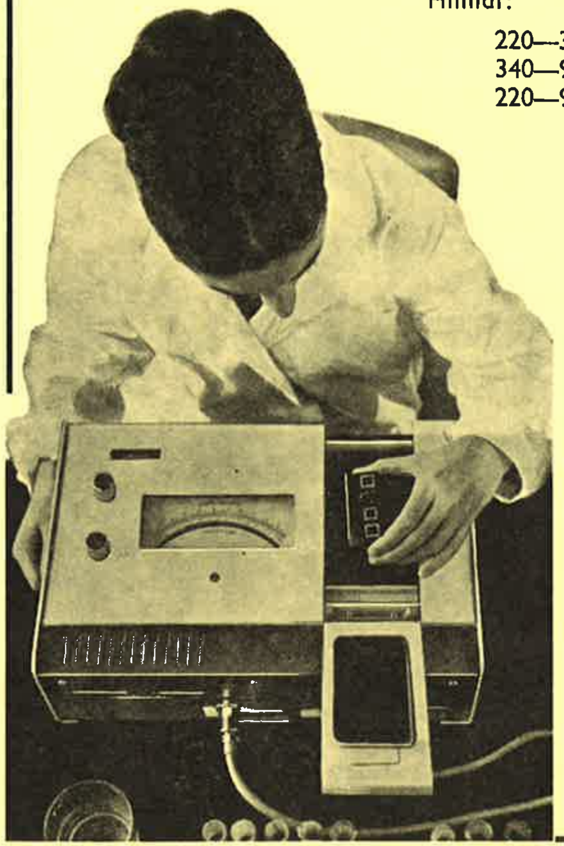

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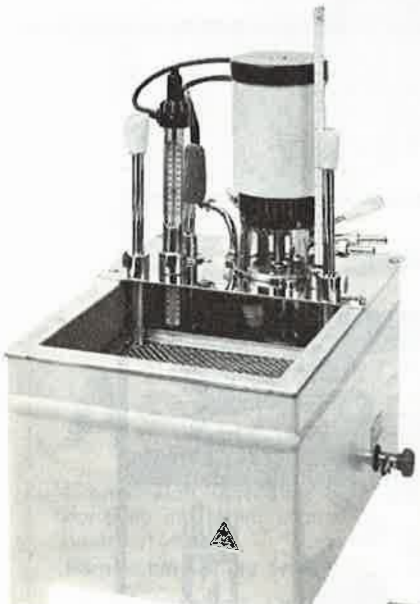

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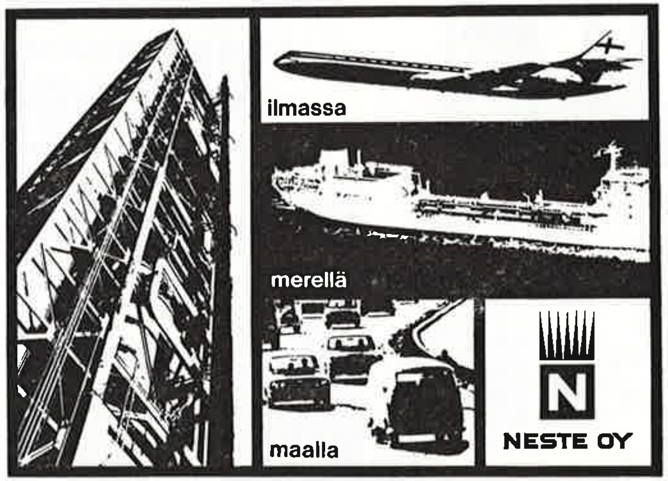
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CONTENTS

EPR studies of compounds related to lignin. Part II. Assignments of the EPR spectra of the cation radicals of isoeugenol and isoeugenol conjugate base.[1]

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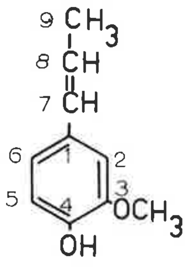
Summary

The cation radicals of isoeugenol and its conjugate base have been prepared with various oxidizing agents, and their EPR spectra have been recorded under various conditions. A hyperfine splitting pattern consisting of $3 \times 2 \times 4$ lines could be assigned to all the spectra. The greatest unpaired spin density is found at the carbon atom *ortho* to the phenolic group and at the β-carbon atom in the side chain. A spin density, about one third of these, is assigned to the α-carbon in the side chain. These coupling constants are slightly dependent on the solvent molecules and the concentration of the substrate. Considerable unpaired spin density is also found at the methyl carbon of the side chain. Very little or no unpaired spin density is assigned to the phenolic oxygen of the radicals studied. The experimental spin density values are found to be in some agreement with theoretical values from PPP-calculations.

The solvent and concentration effects on EPR spectra in solution have not been studied very extensively. Qualitatively we know that the local field at a radical molecule is affected by the diamagnetic shielding of the surrounding solvent molecules, particularly when the radical contains one or more polar groups.[2] Strongly polar solvents can also affect the electron spin state via the spin-orbit coupling as in crystalline solids.

The radical cations of the lignin models isoeugenol (*1*) and its conjugate base (*2*) are the subjects of the present investigation, and solvent effects on the unpaired spin density will be discussed.



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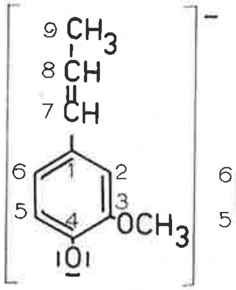

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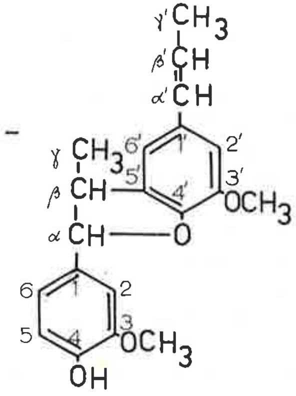

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Results and Discussion

The cation radical of the conjugate base of isoeugenol was obtained either by the demethylation of isoeugenol methyl ether with anhydrous aluminium chloride or antimony pentachloride in electrophilic non-aqueous solvents, or by dissolving isoeugenol in the same reaction mixtures. The over-all demethylation or hydrogen abstraction reaction with aluminium chloride is classically written (ref. 3 pp. 737 and 745):

$$\mathrm{ArOR} + \mathrm{AlCl_3} \rightleftharpoons \mathrm{ArORAlCl_3} \xrightleftharpoons[-\mathrm{RCl}]{\text{heat}} \mathrm{ArOAlCl_2} \overset{-\mathrm{HOAlCl_2}}{\xrightleftharpoons{\mathrm{H_2O}}} \mathrm{ArOH},$$

$\mathrm{R} = \mathrm{CH_3}$ or H.

It is well documented that demethylation of lignin model compounds easily occurs in the *para*-position, and that the *meta*-methoxyl is demethylated under more drastic conditions.[4] The EPR spectra of the isoeugenol conjugate base were identical both when isoeugenol and its methyl ether were used as starting material, and no matter which of the reagents was used, indicating that the same radical species was formed. The cation radical of isoeugenol was obtained by dissolving isoeugenol in concentrated sulphuric or dideuterosulphuric acid.

Aluminium chloride, antimony pentachloride and concentrated sulphuric acid are among other reagents known to yield cation radicals.[5] The solutions of antimony pentachloride in dichloromethane and of aluminium chloride in nitromethane or nitrobenzene showed a broad single line EPR signal (for antimony pentachloride-solvent about 500 G and for aluminium chloride-solvent about 200 G). From this the conclusion is drawn that electron transfer between the solvent and the solute may occur. The signal indicates that the exchange reaction is fast, the effective life-time of the radical species is short. Thus it seems evident that the demethylation and the hydrogen abstraction reactions of isoeugenol methyl ether and isoeugenol respectively are, at least in part, radical reactions initiated by the solvent-catalyst electron exchange ion- or molecule pair. During the whole life-time of the monomeric radical species, classically written $ROAlCl_2$ above, the broad intense background line appears.

The demethylation of isoeugenol methyl ether is fast when antimony pentachloride is used as demethylating agent. No EPR spectrum of the parent compound, isoeugenol methyl ether, could be detected in the reaction mixture, although attempts were made by using varying concentrations of the parent compound and the catalyst.

When aluminium chloride in nitromethane or nitrobenzene was used as demethylating agent, the EPR spectrum of isoeugenol methyl ether cation radical (in the formula above written as $ARORAlCl_3$) was obtained with low concentrations of the catalyst. This spectrum will be discussed elsewhere.[6] Higher concentrations of catalyst yielded different assymetrical spectra, indicating the reaction mixture to contain two or more radical species. Warming of the sample resulted in a 15-line EPR spectrum similar to that of the cation radical of the conjugate base of isoeugenol in antimony pentachloride-dichloromethane solution (fig. 2a). When the reaction mixtures were treated with water and the products isolated after the EPR experiment, the residue consisted mainly of isoeugenol. This was shown chromatographically.

Repeating scans of the EPR spectra of isoeugenol conjugate base showed the signal height increasing for about three hours to about the tenfold, and a considerable narrowing of the spectra could be observed. After about half an hour the hyperfine splitting pattern of the spectrum had completely disappeared. The effects which reduce line widths are discussed by Ayscough.[7] In non-dilute systems, observed line widths are often narrower than predicted. When paramagnetic ions or radicals are brought close together, an exchange interaction is observed, depending on the overlap of the orbitals of the unpaired electrons (exchange-narrowing [7]). From this one might conclude that the concentration of the radical species increases for about three hours. Naturally, other reactions may also take place in the mixture. Dilution of the samples did not, however, diminish the narrowing effect.

Due to the broad back-ground line and the narrowing of

the EPR signals, no attempt will be made in this connection to calculate the spin concentrations and the kinetics of the decay of the radical species. On the other hand an effort will be made to describe the effect of the solvent and the concentration of the substrate and the radical forming catalyst on the unpaired electron distribution in the cation radicals of isoeugenol and its conjugate base.

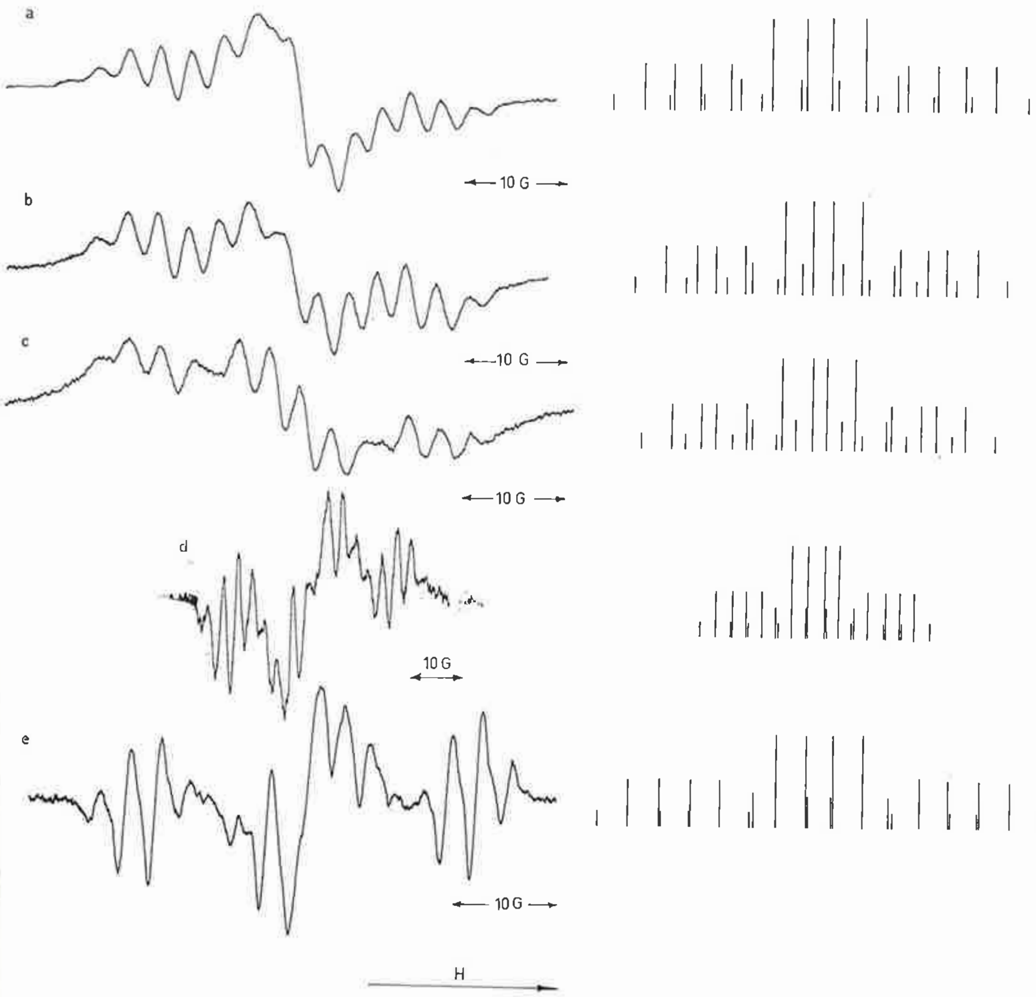


Figure 2. a, b and c show the experimental and the calculated "stick" EPR spectra of isoeugenol conjugate base cation radical, d and e show the experimental and calculated stick spectra of isoeugenol cation radical. For the recording conditions see experimental part.

The discussion is based on fig. 2 showing the EPR spectra of the cation radicals of isoeugenol conjugate base in antimonypentachloride-dichloromethane solution at different concentrations (a, b and c) and of isoeugenol in concentrated sulphuric acid (d) and dideuterosulphuric acid (e). The »stick spectra» at right in the figure are based on the estimated coupling constants listed in table 1. The experimental coupling constants are estimated by comparing with the figures given by Poole [8] for analysis of overlapping resonant lines.

Table 1. Experimental coupling constants calculated from the EPR spectra in fig. 2 (a, b, c, d, and e) and from the EPR spectrum of the cation radical of isoeugenol conjugate base in nitrometane with anhydrous aluminium trichloride as oxidizing agent (f). The spectra were recorded immidiately after mixing the samples.

Coupling constants	$a_8^H = a_5^H$	a_7^H	a_9^H	Total width	
Spectrum					
a	12.8	5.9	2.9	40.7 G	± 0.2 G
b	11.2	5.0	2.9	37.5 G	± 0.2 G
c	10.8	4.4	2.9	35.5 G	± 0.2 G
d, e	14.7	5.9	2.9	45.5 G	± 0.4 G
f	14.5	5.9	2.9	45.2 G	± 0.2 G

It seems evident that the splitting pattern in all the spectra is a 3 × 2 × 4 splitting. For the assignment of the splitting constants of the spectra, the following facts are taken into consideration:

a) the assignment of the EPR spectrum of the anion radical of *trans*-1-phenyl-1-propene,[1]

b) the types of linkages and the way they are formed in the dimeric lignin model dehydro-diisoeugenol (*3*) and in soft wood lignins (for a review see for instance ref. 9) and

c) the results of theoretical calculations using the Pariser-Parr-Pople (PPP) method [10] (fig. 3).

Thus, in *trans*-1-phenyl-1-propene Tylli and the present author were able to show the non-equivalence of the ethylenic protons and the ring protons, as well as the considerable coupling with the side chain methyl protons.[1] Furthermore, the lignin molecule is assumed to be formed by a mechanism involving several steps, the initial being the formation of the cation radical of coniferyl alcohol conjugate base by enzymatic dehydrogenation, the second step involving the recombination of two monomeric radicals, followed by rearrangement to a quinone methide structure, addition of hydroxylic compounds, radicals or other quinone methides. As in dehydro-diisoeugenol (*3*) the carbon-carbon bonds in lignin are linkages between carbon atoms at position 5 in the aromatic nuclei, and the β-carbon atoms of the side chains (5—5′-, 5—β′- and β—β′-linkages).[9]

Considering this it seems natural to assign the greatest coupling constants (the triplet splitting pattern) to the protons at carbon atoms 5 and 8 (for the numbering of the carbon atoms see *1*, *2* and *3*). They are found to be equivalent in all the cases. The second coupling constant (the doublet splitting pattern) is assigned to the proton at carbon atom 7, due to the reactivity of this position [9] and to the fact that the same splitting pattern can be applied to the isoeugenol and its conjugate base spectra.

The third coupling constant (the quartet splitting pattern) invariably about 2.9 G in all the cases, is assigned to the side chain methyl protons, and not to the *meta*-methoxyl protons. This side chain methyl splitting is comparable to that of the methyl protons in *trans*-1-phenyl-1-propene (4.35 G).[1] Although no splitting could be assigned to the *meta*-methoxyl protons in this case (less than 0.2 G) this group must have a significant effect on the unpaired spin density distribution in the molecule, since attempts to record the EPR spectra of the cation radicals of *para*-methoxy-β-methyl styrene, *para*-hydroxy-β-methyl styrene and the conjugate base of the latter under similar conditions as above, only resulted in completely unresolved single line signals. In accordance with this Lindberg, Penttinen and the present author [11] in a polarographic investigation of compounds related to lignin were able to establish the stabilizing effect in an aromatic substitution reaction of the methoxyl group *ortho* to the phenolic hydroxyl. This effect will be the subject of further investigations.

Steelink *et al.*[12,13] state that no cation radicals are formed from guaiacylic compounds by the oxidation with lead dioxide in an inert atmosphere, but that syringol derivatives do give radicals under the same conditions. For monomeric cation radicals of syringol derivatives with a carbonyl group α to the aromatic ring in the side chain Steelink [12] estimated a methoxyl splitting of about 1.30 G, and for the methoxyl protons in the radical syringoxyl Steelink *et. al.* found the methoxyl proton splitting to be 0.76 G.[13]

The hyperfine splitting of the protons at carbon atoms with polarizable linkages to the neighbouring atoms (5,7 and 8) are dependent of the concentration in antimony pentachloride-dichloromethane mixtures. The coupling constants increase with increasing concentration. With higher concentrations than in figure 2a, only the triplet envelope of the spectrum is recorded, lower concentrations than in figure 2c give spectra of very low intensity. The concentration of the catalyst is not critical. No concentration dependence could be found when aluminium chloride was used as oxidizing agent. The spectra of isoeugenol cation radical in sulphuric acid and dideuterosulphuric acid are also independent of the concentration.

The hyperfine splitting of the protons in the positions 5,7 and 8 is slightly dependent on the solvent used. The change in the splitting is not uniform for all the nuclei. This effect is dependent on:

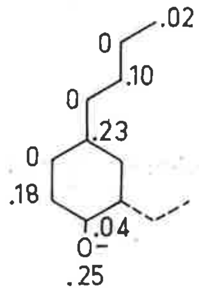
a) the spin-lattice relaxation time, that is a measure of how the spin system is connected to the surrounding »lattice» (solvent),

b) the g-anisotropy by the local electric fields of the solvent ions or molecules,

c) exchange processes discussed formerly, and

d) the formation of ion pairs in the solution. These phenomena are discussed by Ayscough,[7] but, as he points out, despite a large volume of literature on this subject, current interpretations leave much to desire.

Concerning the intricate question of the unpaired electron spin density at carbon atoms 1,3 and 4 and at the oxygen atoms the following conclusions might be drawn. The total width of the EPR spectra is considerably greater than the theoretically and experimentally estimated values for the splitting pattern of one electron.[7] The widths of the spectra are listed in table 1. The appropriate value for $\left|Q^{H}_{CH}\right|$ for spin density calculations is not easy to estimate, but data suggest that the value varies in for instance polynuclear aromatic hydrocarbons between 28 G and 32 G, and it is rather greater for cations than for anions.[5] This complication is at least in part due to the insensitivity to the sign of the electron spin, predicting negative spin densities on part of the nuclei. Anyhow there will not be much spin density left for the atoms mentioned above and the reactivity of the phenolic oxygen must depend on other effects than unpaired spin density.



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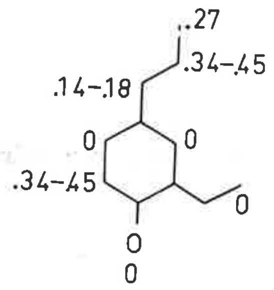

Present
investigation

Figure 3 shows the spin densities calculated with the PPP-method by Mårtenson *et.al.*[10] and the experimental values in the present investigation using the value — 32 G for Q^{H}_{CH} in the McConnell relation.[7] Concerning the experimental values there still remains some uncertainty, due to the poor resolution of the EPR spectra.

Experimental

All the experiments were repeated several times. The EPR spectra were recorded on a Varian E3 instrument. Several spectra of each sample were recorded under varying recording conditions. The spectra in figures 2a, b and c have been recorded under similar recording conditions, lowest possible microwave power (1 mW) with a modulation amplitude of 100 mG and sweep speed 50 G in 30 min. at 9,25 GHz microwave frequency. Spectrum 2 e had a modulation amplitude of 200 mG. Spectrum 2 d was run with sweep speed 100 G in 30 min., microwave power 10 mW and modulation amplitude 500 mG. The sample cell was a flat quarts cell, 0.9 mm thick, immersed in a Dewar container in the resonant cavity. Cooling of the samples to about −60°C gave signals of very low intensity and poor resolution, warming of the samples made the decay of the radical very fast. Spectra were run immediately after mixing the samples. The spectra, in common with most EPR spectra nowadays, have been recorded as the first derivatives of the absorption curves.

Spectrum a in fig. 2 was run on a sample of 1 ml 0.05 M isoeugenol methyl ether in dichloromethane mixed with 0.5 ml 0.2 M antimony pentachloride in dichloromethane.

Spectrum b in fig. 2 was run on a sample of 0.5 ml 0.05 M isoeugenol methylether, diluted with 0.5 ml dichloromethane and mixed with 0.5 ml 0.2 M antimony pentachloride in dichloromethane.

Spectrum c in fig. 2 was run on a sample of 0.125 ml 0.05 M isoeugenol methyl ether diluted with 0.875 ml dichloromethane and mixed with 0.5 ml 0.2 M antimony pentachloride in dichloromethane.

Samples of the cation radical of isoeugenol conjugate base prepared with aluminium chloride were made as follows. 10,20, 50 and 100μ l of a 1 % solution of isoeugenol methyl ether in nitromethane or nitrobenzene were mixed with 0.2 ml 10 % aluminium chloride in the appropriate solvent. The samples were warmed in the resonant cavity to 67°C.

The isoeugenol methyl ether was a *Fluka Ag purum* quality sample distilled 3 times on a fractionating column at 127.5—128°C/8 mm. The isoeugenol was a practical grade product from *Eastman Kodak Co*, distilled on a fractionating column immediately before use, bp. 131.8/10 mm Hg.

In the samples of isoeugenol and isoeugenol methyl ether both the geometrical isomers were present.

Spectra of the cation radical of isoeugenol were run after mixing varying volumes of freshly distilled isoeugenol in 0.5 ml concentrated sulphuric acid or dideuterosulphuric acid, in fig. 2 d and e the samples contain 20 μl isoeugenol respectively.

Dichloromethane was a *Merck Ag* reagent grade product, stored over *Molecular Sieve 4 A*.

Nitromethane and nitrobenzene were *Merck Ag*, practical grade, purified according to ref. 14.

Antimony pentachloride was a *BDH* product, reagent grade, and used without further purification.

Aluminium trichloride, *Merck Ag* practical, was sublimed *in vacuo* before use.

Sulphuric acid was a *Merck Ag Suprapur* product, dideuterosulphuric acid from the same source had a concentration of 96—99 % and a degree of deuteration at least 99 %.

Acknowledgement. The author is indebted to Professor Pekka Kivalo at the Technical University in Otaniemi for kindly permitting me to perform the EPR measurements on the Varian E3 spectrometer in his laboratory.

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EPR studies of compounds related to lignin. Part III. The cation radical of isoeugenol methyl ether.[1]

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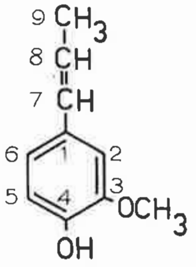
Summary

The cation radical of isoeugenol methyl ether has been prepared in concentrated sulphuric acid, in concentrated dideuterosulphuric acid and in a mixture of aluminium chloride in nitromethane or nitrobenzene. A hyperfine splitting pattern of 3 × 2 × 7 lines could be assigned to the spectra in sulphuric acid, and a hyperfine splitting pattern of 3 × 2 × 4 × 4 lines to the spectra in aluminium chloride-solvent mixtures. The greatest spin density was found at the carbon atom in position 5 in the aromatic nucleus and at the α-carbon atom in the side chain. A spin density about one third of this was assigned to the β-carbon atom in the side chain. Considerable unpaired spin density was also found at the side chain methyl group carbon atom and at the methoxyl carbon atom in the 4-position in the ring. No unpaired spin density could be assigned to the carbon atom in the methoxyl group in the 3-position and to the carbon atoms 2 and 6 in the aromatic ring. The mechanism for the demethylation of the 4-position with an electrophilic metal halide as the demethylating agent, is discussed.

The cation radicals of isoeugenol (*1*) and its conjugate base have been discussed in a previous paper.[1] In order to further establish the assignments of the EPR spectra of these compounds the author investigated the cation radical of isoeugenol methyl ether (*2*).



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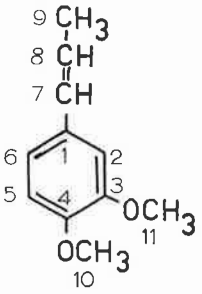

2

The formation of radical cations has been reviewed by Vincow.[2] A great variety of reagents have been used to prepare cation radicals by the oxidation of π-electron containing molecules. Among these the present author tried lead dioxide in an inert atmosphere according to the method used by Steelink *et al.*[3] for the oxidation of lignin model compounds; aluminium chloride in nitromethane as reported by Forbes and Sullivan [4] and in nitrobenzene; antimony pentachloride in dichloromethane used before by, among others, Lewis and Singer;[5] concentrated sulphuric acid and concentrated dideuterosulphuric acid, alkaline aqueous potassium ferricyanide, ceric sulphate in aqueous sulphuric acid, and titanium trichloride in dilute hydrogen peroxide. The four last mentioned reagents are very commonly used in the preparation of cation radicals.

Results and Discussion

The cation radical of isoeugenol methyl ether (*2*) was obtained by dissolving the substrate in concentrated sulphuric or dideuterosulphuric acid, or a mixture of aluminium chloride in nitromethane or nitrobenzene. The EPR absorption of the solutions suggests that singly charged positive ion radicals are responsible for at least part of the observed paramagnetism. The use of the other reagents mentioned above resulted in either the degradation of the radical species as reported formerly [1] or solutions containing no paramagnetic species.

The concentration of the radical in the solutions under consideration requires some discussion. As stated previously [1] it is not possible to estimate the exact values of the concentration with the spectrometer in question (Varian E3). In concentrated sulphuric acid the formation of proton adducts is a competing process which will in general lower the yield of radical cations in that medium. Concentrations less than 1 % have been reported.[4,6] As compared with the intensity of the signal exhibited by isoeugenol in concentrated sulphuric acid, the signal intensity of isoeugenol methyl ether in the same medium is more than tenfold. Concerning the radical concentration in aluminium chloride-nitromethane mixtures Forbes and Sullivan [4] state that the radical formation in this medium is much more complete, up to 100 %. In the cases of isoeugenol methyl ether and the conjugate base of isoeugenol the situation agrees well with these results, since the signal intensities are much greater (at least one hundred times) in the latter medium than in concentrated sulphuric acid.

The EPR spectra of the radical under consideration in sulphuric acid and in dideuterosulphuric acid are practically identical; the conclusion may be drawn that the radical species does neither undergo protonation nor deuteration in positions giving EPR splitting. A hyperfine splitting pattern of 3 × 2 × 7 lines could be assigned to the spectra in these media. All the 42 lines are recognizable in these spectra, either as shoulders or as distinct lines. The assignment for the EPR spectra of the radical cation of isoeugenol methyl ether in mixtures of aluminium chloride-solvent differs from that of the radical in sulphuric acid. By calculation of the "stick" spectra the hyperfine splitting pattern was found to be a 3 × 2 × 4 × 4 splitting. As will be shown the difference is not, however, very far reaching. Spectra in nitromethane and nitrobenzene were identical.

Table 1. Experimental coupling constants calculated from the spectra in fig. 2, a) for the cation radical of isoeugenol methyl ether in concentrated sulphuric acid, b) for the radical in dideuterosulphuric acid and c) for the radical in aluminium chloride-nitromethane mixture. For the numbering of the carbon atoms see figure 1. For the recording conditions see experimental part. The spectra were recorded immediately after mixing.

Coupling constants	$a_5^H = a_8^H$	a_7^H	a_9^H	a_{10}^H	Total width	
Spectrum						
a, b	13.05	4.2	3.1	3.1	48.7	± 0.1 G
c	9.7	3.5	2.6	1.75	34.3	± 0.2 G

In the EPR spectrum of the cation radical of isoeugenol (*1*) the triplet in the splitting pattern of 3 × 2 × 4 lines was interpreted as being the splitting of the protons at carbon atoms 5 and 7 (for the numbering of the carbon atoms see *1* and *2*).[1] Accordingly, the triplet in the spectra under consideration is assigned to the corresponding protons (the protons at carbon atoms 5 and 7) in the methylated compound. The coupling constants are listed in table 1. In the same way the second coupling constant (the doublet splitting pattern) is assigned to the corresponding protons in compounds *1* and *2* (the proton at carbon atom 7). The non-equivalence of the ethylenic protons in substituted phenyl ethylenes has been shown previously.[7]

With respect to the third coupling constant (the septet splitting pattern) in the spectrum in sulphuric acid the conclusion is drawn that it is due to coupling between the unpaired electron and the protons in the side chain methyl group (carbon atom 9) and the protons in the methoxyl group in *para*-position to the side chain (carbon atom 10). The double quartet splitting of the spectrum in aluminium chloride-solvent mixtures seems in accordance with this to be due to coupling with the protons in the side chain methyl group (carbon 9) and the *para*-methoxyl protons (carbon 10) respectively, the protons of the two groups being nonequivalent with each other.

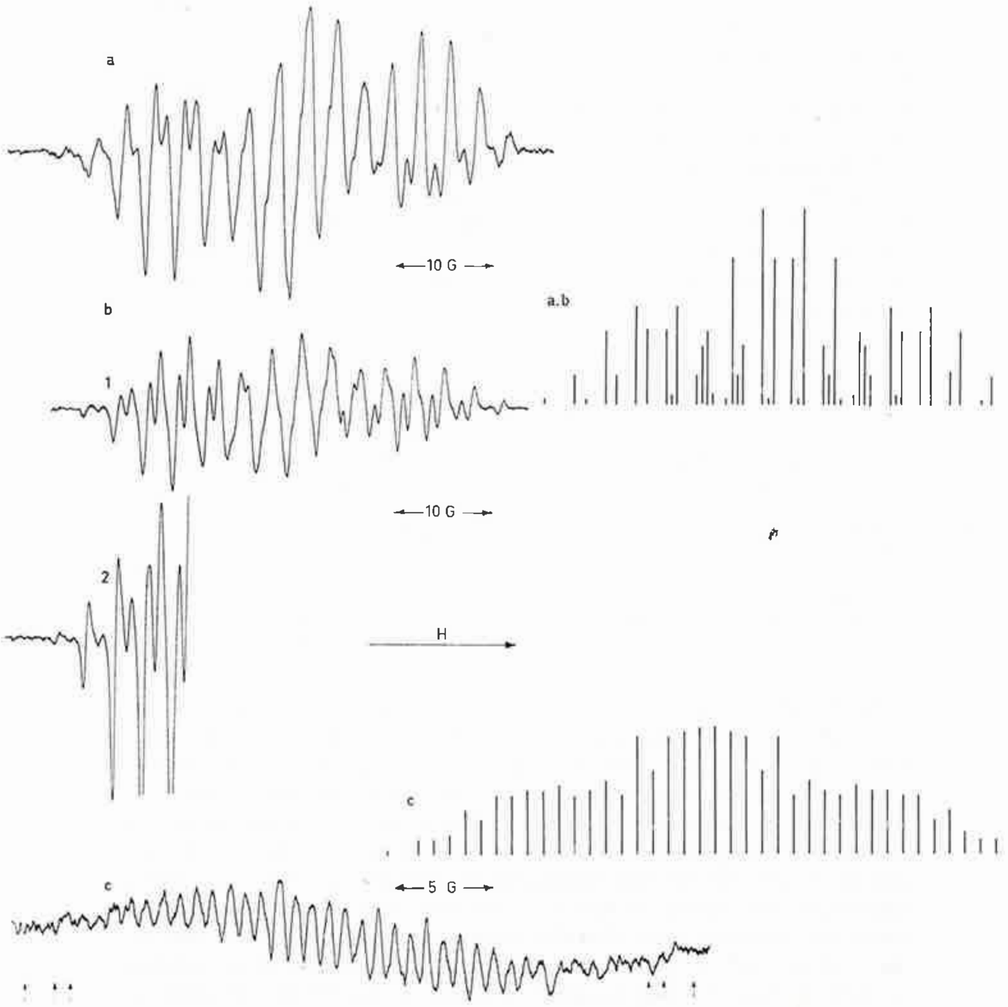

Figure 2. a) shows the experimental and the calculated "stick" EPR spectra of the cation radical of isoeugenol methyl ether in sulphuric acid, b) shows the experimental and the calculated "stick" spectra of the radical in dideuterosulphuric acid, including part of the spectrum run with higher modulation amplitude, and c) shows the experimental and the calculated "stick" spectra of the radical in nitromethane-aluminium chloride mixture. For the recording conditions see the experimental part. The spectra are recorded as the 1:st derivatives.

Very little or no proton splitting (less than 0.2 G) could be assigned to the protons in the *meta*-methoxyl group (carbon atom 11). The conclusion that the *meta*-methoxyl carbon atom has very little unpaired spin density is based mainly on the

following facts. In the series of Hammet σ values for substituents in the aromatic ring the values for the methoxyl groups are $\sigma_p = -0.27$ and $\sigma_m = +0.12$ respectively.[8] (In a recent investigation Bowers [9] estimated σ_p values for a number of substituents, basing the results on EPR data. For the *para*-methoxyl group Bowers gives the value $\sigma_p = -0.16$.) The different signs of σ_p and σ_m mean that the *para*-methoxyl group is a weaker electron attractor than a proton, and that the *meta*-methoxyl group is a stronger electron attractor than a proton. The side chain methyl group has electron releasing properties (+I effect).[8] Consequently the side chain methyl group and the *para*-methoxyl group exhibit similar electron releasing properties towards the conjugated π-electron system. Splitting constant values in the literature (*e.g.* ref. 10, for a rewiew see ref. 2) seem to indicate that electron releasing groups substituting aromatic hydrocarbons give rise to a considerable splitting through a $\sigma - \pi$ exchange interaction (spin polarization) mechanism.[2] These facts seem to support the conclusion that the *para*-methoxyl gives rise to proton splitting, whereas the *meta*-methoxyl does not.

Concerning the magnitude of the proton splitting of the side chain methyl group and the *para*-methoxyl group in the spectrum in aluminium chloride-solvent mixture, some uncertainty will remain. The opinion of the present author is that the greater splitting constant (2.6 G) could be the methyl proton splitting, since this value agrees well with the side chain methyl proton splitting in spectra discussed previously [1,7] and with the value 3.1 G for the radical under consideration in sulphuric acid. Accordingly the smaller splitting constant (1.75 G) is assigned to the protons in the *para*-methoxyl group. No coupling (less than 0.2 G) is found for protons at carbon atoms 2 and 6.

The total width of the spectra is greatly dependent on the solvents used. The total width in sulphuric acid and in dideuterosulphuric acid (48.7 G) is much greater than that in nitromethane- or nitrobenzene-aluminium chloride mixtures (34.3 G). In any case the total width is greater than the experimental and theoretical coupling constant for one electron.[11] This means that there will be very little or no unpaired spin density left for the carbon atoms 1,3 and 4 and for the oxygen atoms in the methoxyl groups. This is in accordance with the findings for the isoeugenol cation radical.[1]

It is a well known fact that in the dealkylation of an alkyl aryl diether with an electrophilic metal halide, the first alkyl group is easily abstracted, the second requiring elevated temperature and excess catalyst for the splitting-off reaction.[12] In demethylation experiments of compounds related to lignin it has been shown that demethylation of a methoxyl group in the *para*-position to the side chain easily occurs, whereas the demethylation of the *meta*-situated methoxyl group requires more drastic conditions.[13] In a previous[1] paper the conclusion was drawn that the demethylation of isoeugenol methyl ether is, at least in part, a radical reaction in mixtures of an electrophilic metal halide in an electrophilic solvent. If this conclusion is correct, the unusual stability of the *meta*-methoxyl group towards demethylating agents of this kind, as compared with a similar group in the *para*-position, might be connected to the lack of unpaired spin density in this position.

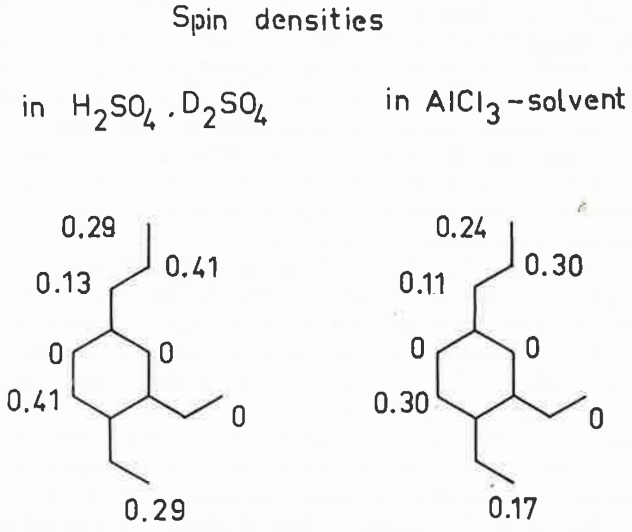

Figure 3 shows the spin densities calculated according to the McConnell relation[11] from the experimental coupling constants in table 1 using the value 32 G for $\left|Q_{CH}^{H}\right|$. For the choice of the value for Q_{CH}^{H} compare ref. 1.

Experimental

All the experiments were repeated several times. The EPR spectra were recorded on a Varian E3 instrument. Several spectra of each sample were recorded under varying recording conditions. The spectra in fig. 2 were run-with lowest possible microwave power (1 mW) at 9.25 GHz microwave frequency. The sample cell was a flat quarts cell, 0.9 mm thick, immersed in a Dewar container in the resonant cavity. Spectra were run immediately after mixing the samples.

Spectrum a in fig. 2 was run on a sample of 3 mg isoeugenol methyl ether in 1 ml concentrated sulphuric acid with 200 mG modulation amplitude at 55°C, sweep speed 100 G in 30 minutes.

Spectrum b 1 in fig. 2 was run on a sample of 1.5 mg in 0.5 ml dideuterosulphuric acid with 50 mG modulation amplitude at 58°C, sweep speed 100 G in 60 minutes. The decay of the radical is observed as diminished intensity at the end of the spectrum. Spectrum b 2 was run on the same sample with modulation amplitude 500 mG, only the low field part of the spectrum is shown.

Spectrum c in fig. 2 was run on a sample of 100 μl 1 % solution of isoeugenol methyl ether in nitromethane, mixed with 100 μl 5 % solution of aluminium chloride in nitromethane, with 100 mG modulation amplitude at room temperature, tveep speed 50 G in 16 minutes.

The isoeugenol methyl ether was a *Fluka Ag purum* quality sample distilled three times on a fractionating column at 127.5—128°C/8 mm Hg. The product was used without the separation of the geometrical isomers.

Nitromethane and nitrobenzene were *Merck Ag* practical grade, purified according to ref. 14.

Aluminium chloride, *Merck Ag* practical, was sublimed *in vacuo* before use.

Sulphuric acid was a *Merck Ag Suprapur* product, dideuterosulphuric acid from the same source had a concentration of 96—99 % and a degree of deuteration at least 99 %.

Acknowledgement. The author is indebted to Professor Pekka Kivalo at the Technical University in Otaniemi for kind permission to perform the EPR measurements in his laboratory.

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Litteratur

Gösta Wranglén: Metallers korrosion och ytskydd
Almqvist & Wiksell, Stockholm, 1967, 304 sid. Inb. Sv.kr. 72:—.

Gösta Wranglén: Korrosionslära
Institut för Metallskydd AB, Stockholm 26, 1967 200 sid. offsettryck. Inb. Sv.kr. 20:—.

Större delen av jordens metaller förekommer i sitt naturliga tillstånd såsom kemiska föreningar, malmmineral, ur vilka metallen utvinnes genom metallurgiska processer. Korrosionen är den motsatta kemiska processen vid vilken metallen eller legeringen strävar att återgå till sitt termodynamiskt mest stabila tillstånd. Därför förekommer också korrosionen nästan överallt där metaller användes och teknikens korrosionsskydd är en ständig kamp mot naturkrafterna.

En sammanfattande framställning om korrosion och korrosionsskydd av metaller har icke hittills funnits på svenska och den år 1960 av Kemiska Centralförbundet utgivna »Korroosio ja sen estäminen» är på grund av teknikens snabba utveckling redan föråldrad. Därför hälsar man också med tillfredsställelse prof. Gösta Wrangléns lärobok, »Metallers korrosion och ytskydd». Arbetet har tillkommit i samband med de föreläsningar i korrosionslära som författaren alltsedan 1959 hållit för studerande inom sektionerna för kemi och bergsvetenskap vid Kungl. Tekniska Högskolan i Stockholm.

Författaren inleder sin framställning med en kortfattad redogörelse för elektrokemins teori samt de elektrodprocesser, som ligger till grund för korrosionsfenomenen. Därför följer metallografins grunder, korrosion i olika miljöer, den elektrokemiska korrosionens kinetik samt vätgasutvecklande och syrgasförbrukande korrosion. I ett antal kapitel studeras i detalj olika korrosionstyper och korrosionsmiljöer. Vidare behandlas olika slag av korrosionsskydd samt korrosionsprovning. Verket avslutas med några empiriska potential-pH-diagram för tekniskt viktiga metaller, allmänna referenser samt ett relativt utförligt alfabetiskt register. Efter varje avsnitt hänvisas till monografier eller andra specialarbeten på området, som i allmänhet följts upp till 1967.

Bokens tema är metallernas korrosion, men i samband med kapitlet om organiska beläggningar redogör författaren även relativt utförligt och sakkunnigt för polymerers och plasters kemiska och mekaniska resistens. Man hade därför väntat sig en lika utförlig redogörelse för cements och betongs egenskaper och skyddande verkan, så vitt undertecknad kunnat se har dessa frågor icke behandlats i något speciellt avsnitt, trots att de är av stor betydelse för armerade betongkonstruktioners hållfasthet. Likaså hade man gärna sett ett kapitel rörande valet av material, där ersättningen av metaller med andra material diskuterats ur teknisk-ekonomisk synpunkt. De gjorda anmärkningarna gäller dock icke sådana frågor, som skulle påverka bokens användbarhet som läro- och handbok. Verkets typografiska utstyrsel är även god.

Boken »Korrosionslära» av samma författare, är en kortfattad översikt över metallers korrosion och ytskydd och utgör en förkortad och teoretiskt förenklad motsvarighet till ovan refererade verk. Den är avpassad för de tekniska gymnasielinjerna och fackskolorna liksom för utbildningskurser inom industriföretag och organisationer. Även plastteknologin och färg- och lackkemin liksom ytbehandlingstekniken refereras i den omfattning, som är nödig för nämnda skolformer. Läroboken torde även med fördel kunna läggas till grund för korrosionsskyddsundervisningen i motsvarande skolformer i vårt land.

Gösta Wranglén har med sina två läroböcker på ett centralt område givit den tekniska undervisningen det stöd den behöver för att med framgång kunna möta det ständigt stigande kvalitetskravet.

J. Johan Lindberg

A. Sheludko: Colloid Chemistry, *Elsevier Publ. Comp., Amsterdam-London-New York, 1966. 277 sid. Ind. 46:00 Fmk.*

Surface Chemistry. Proceedings of the Second Scandinavian Symposium on Surface Activity, Stockholm, November 18—19, 1964. *Redaktion: Per Ekwall, Kjell Groth och Vera Runnström-Reio. Munksgaard, Köpenhamn 1965, 315 sid. inb.*

Utvecklingen på yt- och kolloidkemins område har under de senaste decennierna på grund av de fysikalisk-kemiska mätmetodernas definitiva genombrott gjort mycket stora framsteg och denna gren av kemin uppvisar numera en mycket långtgående teoribildning. I de flesta läroböcker avsedda för högskoleundervisning i yt- och kolloidkemi saknar man dock ett verkligen enhetligt och fysikaliskt-kemiskt grepp på ämnet såsom ett stöd för den ofta mer eller mindre kvalitativa framställningen, trots att det finnes goda monografier att bygga på, såsom t.ex. Kruyt's »Colloid Science».

Sheludko, som är professor i fysikalisk kemi vid universitetet i Sofia och känd kolloidforskare har i sin bok »Colloid Chemistry» försökt giva en teoretisk och enhetlig termodynamisk framställning av ämnet, delvis på bekostnad av det rikliga empiriska och experimentella materialet, som vanligen presenteras i läroböcker av denna typ. Den engelska översättningen är en fullständigt omarbetad version av verkets andra ryskspråkiga upplaga och omfattar följande åtta kapitel: Framställning och rening av lyofoba kolloidala system, kolloidernas optiska egenskaper, kolloidlösningarnas molekylar-kinetiska egenskaper, ytornas fysikaliska kemi, elektrokinetiska fenomen, tunna skikt, lyofoba solers stabilitet, skum och emulsioner. Varje kapitel avslutas med en relativt omfattande litteraturförteckning där de viktigaste rönen i öst och väst t.o.m. år 1963 refereras.

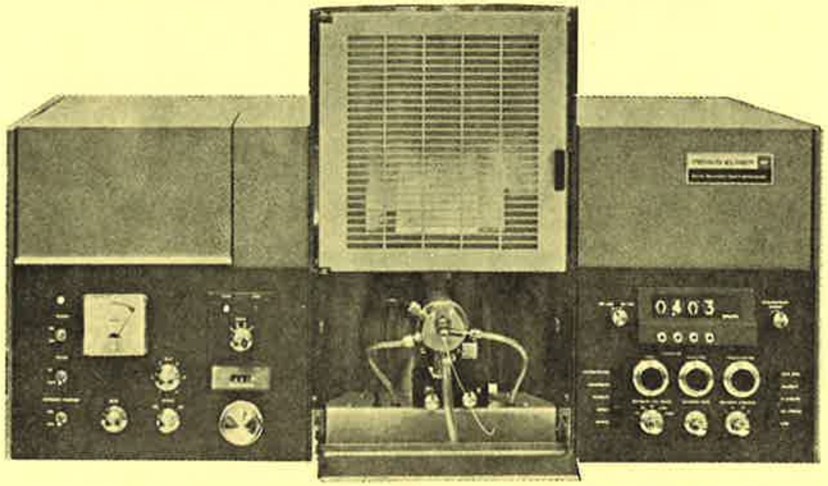
Framställningen är klar och varje kapitel inledes med en kort översikt av undersökningsmetoder och den experimentella situationen varpå följer en enhetlig presentation av fenomenets teori. Författarens strävan synes härvid ha varit att såvitt möjligt förklara de kolloidala och ytkemiska processerna i termodynamiska och molekylar-kinetiska termer. Den matematiska bakgrund, som fordras av läsaren överstiger dock icke den sedvanliga fysikalisk-kemiska grundkursens. Framställningen synes även i flere avsnitt bygga på författarens egna forskningsresultat. Verkets användbarhet ökas även av ett alfabetiskt sakregister.

I verket »Surface Chemistry» ges en sammanfattning av de föredrag och diskussioner, som höllos vid Det Andra Nordiska Symposiet för Ytaktivitet i Stockholm den 18 och 19 november 1964. På grund av det stora antalet meddelanden, som avgavs under symposiet och den livliga debatten, som följde, blev symposiets tidsschema starkt rubbat. Med föreliggande bok strävar symposiets ledning att korrigera de därav följande informationssvårigheterna och samtidigt öka och sprida intresset för ytkemi.

Med sina 25 föredrag och 315 sidor ger verket en imponerande bild av den ytkemiska forskningens omfattning och djup i Norden. De närmare fem år, som gått sedan symposiet, har även visat att arrangörernas förhoppningar inte kommit på skam.

J. Johan Lindberg

Innehåll 1969 Sisältö



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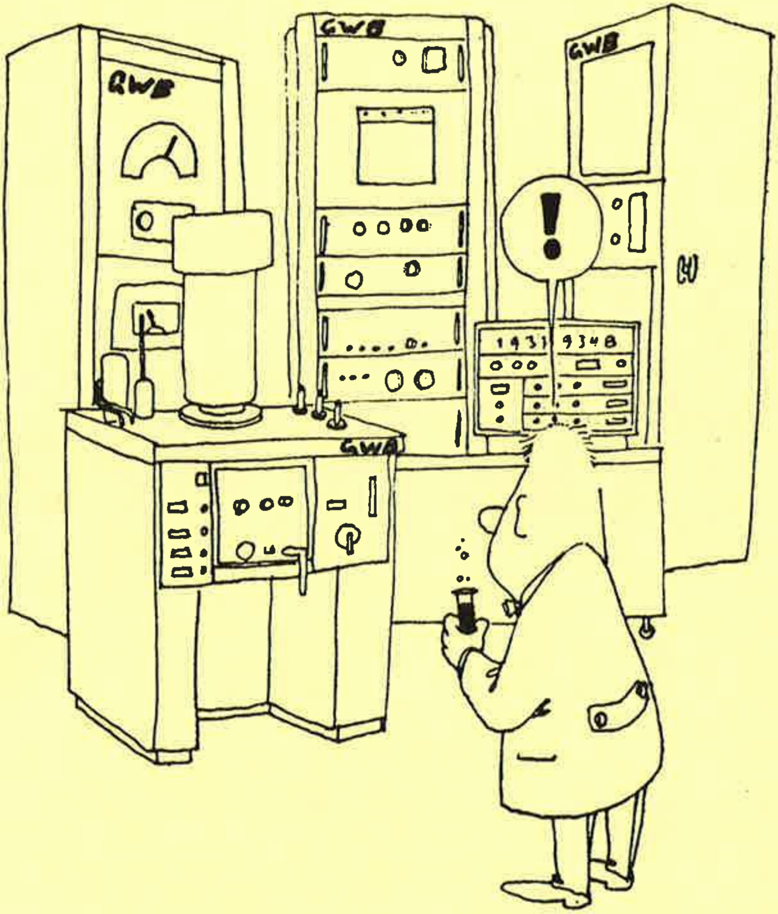

Frenckellska Tryckeri Ab, Helsingfors 1969