

CONCLUSION

1. The phenoxy radicals formed as the result of the electrochemical oxidation of lignin are extremely unstable and are capable of immediate recombination.
2. The difference in the donor-acceptor properties of the individual fragments of lignin indicates a thermodynamic probability of the appearance of autocatalytic processes.

LITERATURE CITED

1. E. N. Eremin, Fundamentals of Chemical Kinetics [in Russian], Moscow (1976), p. 375.
2. S. G. Mairanovskii, Ya. P. Stradyn', and V. D. Bezuglyi, Polarography in Organic Chemistry [in Russian], Leningrad (1975), p. 352.
3. L. V. Bronov, É. I. Chupka, V. M. Nikitin, E. N. Kalugin, N. P. Skvortsov, and Yu. V. Vodzinskii, *Chim. Drevesiny*, No. 1, 40 (1960).
4. E. Streitwieser, Molecular Orbital Theory for Organic Chemists, Wiley, New York (1961).
5. V. N. Mikhailov and B. A. Kiselev, *Prib. Tekh. Eksp.*, 6, 308 (1977).
6. F. M. Gizeddinov and E. I. Chupka, Abstracts of Lectures at an All-Union Conference on the Prospects of the Utilization of Lignin in the National Economy [in Russian], Bratsk (1980), p. 41.
7. I. M. Pepper, P. E. Boylis, and E. Adler, *Can. J. Chem.*, 39, No. 8, 1271 (1959).
8. É. I. Chupka, T. A. Khrapkova, and V. M. Nikitin, *Khim. Drevesiny*, 5, 81 (1975).
9. T. M. Kroshilova, E. I. Chupka, and V. M. Nikitin, *Khim. Drevesiny*, 2, 58 (1976).
10. K. V. Sarkhanen and C. H. Ludwig, Lignins, Wiley-Interscience, New York (1971).
11. V. D. Pokhod'ko, A. A. Beloded, and V. D. Komenko, Redox Reactions of Free Radicals [in Russian], Kiev (1977), p. 276.

CORRELATIONS BETWEEN QUANTUM-CHEMICAL AND PHOTO- AND ELECTROCHEMICAL MAGNITUDES IN THE STUDY OF COMPOUNDS MODELING A STRUCTURAL UNIT OF LIGNIN

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Correlations have been established which permit the theoretical prediction and analysis of oxidation-reduction and acid-base properties on the basis of calculated quantum-chemical data for compounds modeling a structural unit of lignin of the guiacyl type.

The use of various physicochemical methods permits the complex solution of questions of the investigation of the reactivity of lignin and of individual model fragments in redox processes. Since lignins are compositionally inhomogeneous, it may be assumed that the rates of oxidation of the individual fragments will be different.

Studies on model compounds have been widely used in the investigation of the reactivity of lignin. However, no systematization of the properties of model compounds that could be carried out in the form of correlations between the oxidation (reduction potentials) and the energies of the highest occupied (lowest vacant) molecular orbitals, respectively, calculated by the method of quantum chemistry in various approximations, has been performed.

The existence of a correlation shows that the physicochemical properties of the model compounds being analyzed are satisfactorily described by reactivity indices obtained by the quantum-chemical method (within the limits of the parametrization used) and can subsequently be employed for the theoretical analysis of those model compounds the experimental investiga-

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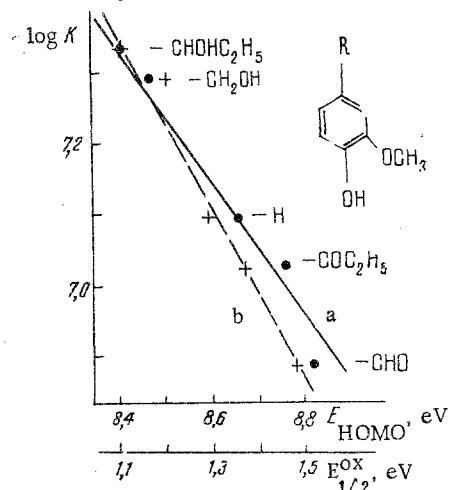


Fig. 1

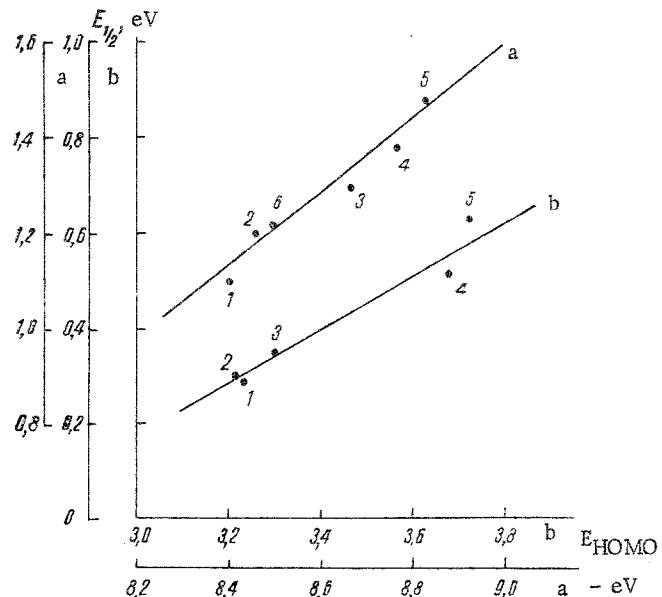


Fig. 2

Fig. 1. Correlation relationships between the logarithm of overall rate constant of the reaction of compounds modeling lignin with oxygen and the HOMO energies (a) and the oxidation potentials, $E_{1/2}$, (b) corresponding to them.

Fig. 2. Correlations between the oxidation potentials $E_{1/2}$ and the HOMO energies for the molecular (a) and ionic (b) forms of compounds modeling lignin: 1) α -guaiacylpropanol; 2) vanillyl alcohol; 3) guaiacol; 4) α -guaiacylpropanone; 5) vanillin; 6) ferulic acid.

tion of which comes up against considerable methodological difficulties (in particular, quinones and quinone methides, free radicals, etc., i.e., unstable, energy-rich, compounds). However, in the use of mathematical methods the research worker must be convinced of the correctness of the information given by them. In view of factors difficult to take into account (solvation effect, the influence of intra- and intermolecular hydrogen bonds), it is by no means always possible to obtain a satisfactory agreement of the results between calculated and experimentally determined magnitudes reflecting the physicochemical properties of the compounds.

We have made an attempt to analyze the extent to which it is justified to use:

modeling in the investigation of the kinetics of the homogeneous oxidation of compounds modeling a structural unit of lignin, in particular, in the sensitized oxidation by singlet oxygen, on the basis of results obtained by electrochemical methods; and

the methods of quantum chemistry for the numerical evaluation of the reactivities of model compounds in oxidation-reduction processes.

It is generally known that the rate constants of an oxidation (reduction) reaction are in exponential dependence on the potential of the system (the difference in the potentials of the substrate and the reagent) [1]. Thus, if the individual model compounds differ by their oxidation potentials, then on oxidation by the same reagent (in the present communication, oxidation by singlet oxygen is considered), differences in the rates of their oxidation will also be observed.

Since oxidation and reduction potentials (if they are close to the thermodynamic magnitudes) are determined by the magnitudes of the energies of the HOMO (LUMO), then, provided that the experimentally determined magnitudes are correct and the calculations are valid, correlations should be observed between the $E_{1/2}$ values of the oxidation potentials ($E_{1/2}$ values of the reduction potentials) and the HOMO (LUMO) energies [2]. An attempt by Kratze et al. to find a sufficiently strict correlation between the magnitudes of the "critical" oxidation potentials of model compounds and of the energy of the HOMO proved to be unsuccessful.

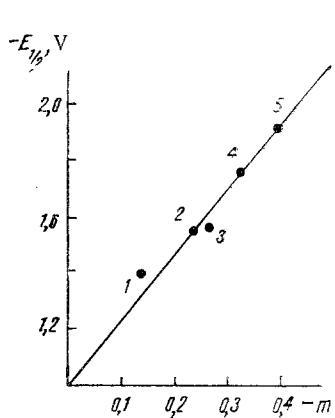


Fig. 3

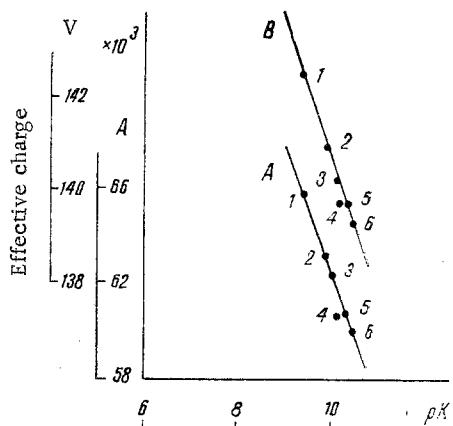


Fig. 4

Fig. 3. Correlation between the reduction potentials $E_{1/2}$ and the HOMO energies (by the MO LCAO method in the Huckel approximation) for the following compounds: 1) rosolic acid; 2) p-benzoquinone; 3) cinnamaldehyde; 4) vanillin; 5) α -guaiacylpropanone.

Fig. 4. Correlations of the positive π -charges of the oxygen atom A) and of the σ -charge of the hydrogen atom B) with the pK values of the phenolic hydroxyl of compounds modeling lignin: 1) ferulic acid; 2) guaiacol; 3) isoeugenol; 4) vanillyl alcohol; 5) eugenol; 6) α -guaiacylpropanol.

ful [3], probably because of the fact that the "critical" oxidation potential determined by a method suggested by Fieser [4] does not correspond to the thermodynamic value of the oxidation potential.

On comparing the results obtained by the method of flash photolysis in the dye methylene blue sensitized photooxidation of the compounds modeling lignin by singlet oxygen and by the method of oscillographic voltammetry, we observed a correlation the logarithm of the rate constant with the oxidation potential and also with the energies of the HOMO (calculated by the CNDO/S method) of the model compounds (Fig. 1).* The correlation coefficient between the magnitudes of $\log K$ and the HOMO energies (curve 1) is 0.97, and that between $\log K$ and the oxidation potential is 0.99 (curve 2).

The value of K for the model compounds investigated were as follows: vanillin, $0.78 \cdot 10^7$; α -guaiacylpropanone, $1.08 \cdot 10^7$; guaiacol, $1.25 \cdot 10^7$; vanillyl alcohol, $1.91 \cdot 10^7$; and α -guaiacylpropanol $2.14 \cdot 10^7$ liter \cdot mole $^{-1}$ \cdot sec $^{-1}$. The existence of a strict correlation between the logarithm and the rate constant of the oxidation of the model compounds by singlet oxygen in solutions and the values of the oxidation potentials $E_{1/2}$ and of the HOMO shows the validity of the use of methods of electrochemical oxidation at solid anodes for investigating kinetics in the modeling of homogeneous oxidation reactions.

Completely satisfactory correlations both for the molecular and for the ionized forms of the compounds modeling lignin have been found between the oxidation potentials $E_{1/2}$ at a graphite electrode and the HOMO energies calculated by the CNDO/S method (Fig. 2). The correlation coefficient for the ionic form is 0.99, and for the molecular form 0.93. A correlation has also been found between the reduction potential $E_{1/2}$ of a number of model compounds at a dropping mercury electrode and the LUMO energies (calculated by Huckel's method), the correlation coefficient for this case being 0.99.

Consequently, it may be considered that the experimentally determined oxidation and reduction potentials are close to the values of the thermodynamic potentials, and quantum-chemical methods give complete correct calculated results.

*The experiments on flash photolysis were performed by F. M. Gezitdinov.

Since the $E_{1/2}$ potentials of the oxidation and reduction of phenols, aldehydes, ketones, quinones, and quinone methides mentioned [5] depend on the pH of the solution, it must be expected that the rate of oxidation (or reduction) will obey the laws of acid-base catalysis. Consequently, particular interest is presented by an investigation of the acidity of the phenolic hydroxyl in the various fragments of lignin as functions of their structure.

The results of quantum-chemical calculations enable us to judge the acid-base properties of compounds modeling lignin. This follows from the existence of established correlations between the experimentally determined values of pK for the phenolic hydroxyl and the π -charge of the oxygen atom and the σ -charge of the hydrogen atom of the phenolic hydroxyl calculated by the CNDO/S method for a series of compounds modeling a structural unit of lignin [6]. The correlation coefficients have values of 0.96 and 0.98, respectively. However, the values of the charges are not always an absolute measure of the acidities of all types of phenols; consequently, the relationships obtained permit an approximate evaluation of the pK value of the phenolic hydroxyl on the basis of the quantum-chemical calculations only for compounds modeling a structural unit of the guaiacyl type.

EXPERIMENTAL

The overall constant of the reaction of compounds modeling lignin with singlet oxygen, $K = k_r + k_g$ (where k_r and k_g are, respectively, the constants of the chemical and physical quenching of singlet oxygen) were determined by flash photolysis in n-butanol from the dependence of the yield of phenoxy radicals on the initial concentration of the phenols under investigation [7], which has been used previously by Thomas and Foote [8]. As the sensitizer of singlet oxygen we used methylene blue.

Electrochemical oxidation was carried out for the ionic form in 1 M NaOH. Graphite of type OSCh 7-4 was used as the working electrode. To decrease its porosity and cut down residual currents, the graphite was impregnated with a mixture of paraffin wax and polyethylene (1:1) in vacuum for 6 h. The comparison electrode was a saturated calomel half-cell. The volt-ampere curves were recorded on a PO 5122 polarograph in the differential regime with photographic recording. For the molecular forms, oxidation was carried out in acetonitrile with 0.1 M LiClO₄ as the supporting electrolyte. The working electrode was of platinum and graphite with mechanical renewal of the surface. The comparison electrode was Ag/0.1 N AgNO₃/0.1 N LiClO₄. All potentials are given relative to the saturated calomel electrode. The half-wave oxidation potentials have been corrected for the rate of scanning.

Polarogram of model compounds in 1 N LiOH solution were recorded in a three-electrode cell at a dropping mercury electrode with the aid of an alternating-current polarograph (PPT-1). The characteristics of the capillary were $m^{2/3} t^{1/6} = 2.5 \text{ mg}^{2/3} \cdot \text{sec}^{-1/2}$. Before a polarogram was recorded, purified argon was passed through the solution for 15-20 min. The concentration of the model compound in the solution amounted to $1 \cdot 10^{-3} \text{ M}$.

Quantum-chemical calculations taking into account σ - and π -electron subsystems* were performed by the SCF MO LCAO method (the self-consistent field of the molecular orbitals in the form of a linear combination of atomic orbitals) in the approximation of complete neglect of differential overlap (CNDO) with spectroscopic parametrization [9] according to a program realizing a variant of the method described by Shchegoleva et al. [10]. The parameters of the C, H, O system were taken from the literature [10, 11] and are given below.

The spectroscopic parameters of the CNDO/S method are given below (eV):

Atoms	ρ_A^0	γ_{AA}	$I_s + A_s$	$I_p + A_p$
H	12.00	12.85	14.35	—
C	17.50	10.93	29.92	.61
O	45.00	15.97	54.51	21.93

where ρ_A^0 are the bonding parameters; γ_{AA} are the one-center Coulomb integrals; and $I_s + A_s$ and $I_p + A_p$ are the orbital electronegativities for the s and p orbitals, respectively.

Calculations taking into account only the π -electron subsystem were performed by the MO LCAO method in Huckel's approximation. The following parameters were used for the cal-

*The calculations were performed by A. Yu. Punka on a BES computer using a program proposed by I. I. Zakharov.

culation: $\alpha_{C=O} = \alpha_{C-C} + \beta_{C-C}$; $\beta_{C=O} = \beta_{C-C}$; $\alpha_{OH} = \alpha_{C-C} + 2\beta_{C-C}$; $\beta_{OH} = 0.8 \beta_{C-C}$; $\alpha_{OCH_3} = \alpha_{C-C} + 2\beta_{C-C}$; $\beta_{OCH_3} = 0.7 \beta_{C-C}$ [2].

CONCLUSION

The existence of a correlation between the reactivity indices calculated by quantum-chemical methods (CNDO/S and Huckel) and certain physicochemical parameters of the oxidation-reduction and acid-base properties of compounds modeling the structural unit of lignin has been established. This permits theoretical prediction and analysis of these properties on the basis of calculated quantum-chemical figures for compounds of the guaiacyl type modeling lignin.

LITERATURE CITED

1. Yu. V. Pleskov, *The Rotating Disk Electrode*, Consultants Bureau (1976).
2. E. Streitwieser, *Molecular Orbital Theory for Organic Chemists*, Wiley, New York (1961).
3. K. Kratze, P. Glays, W. Lonsky, and J. Gratzl, *Wood Sci. Technol.* 8, 35 (1947).
4. F. L. Fieser, *J. Am. Chem. Soc.*, 52, No. 12, 5204 (1930).
5. S. G. Mairanovskii, Ya. P. Stradyn', V. D. Bezuglyi, *Polarography in Organic Chemistry*, Plenum Press (in press).
6. V. B. Karklin', A. Yu. Punka, and E. I. Chupka, *Abstracts of Lectures at an All-Union Conference on Prospects for the Utilization of Lignin in the National Economy* [in Russian], Bratsk (1980), p. 43.
7. F. M. Gizeddinov and E. I. Chupka, *Abstracts of Lectures at an All-Union Conference on Prospects for the Utilization of Lignin in the National Economy* [in Russian], Bratsk (1980), p. 41.
8. M. J. Thomas and G. S. Foote, *Photochem. Photobiol.*, 27, No. 6, 683 (1978).
9. J. Del Behe and H. H. Jaffe, *J. Chem. Phys.*, 48, No. 4, 1807 (1968).
10. L. N. Shchegoleva, I. I. Zakharov, and Yu. A. Kruglyak, *A Study of the Electronic Absorption Spectra of Naphthalene and Some of Its Fluorine Derivatives by the CNDO/Q Method. Preprint ITF-78-63 R* [in Russian], Kiev (1978).
11. G. Kuehnlenz and H. H. Jaffe, *J. Chem. Phys.*, 55, No. 6, 2238 (1973).

USE OF KOVATS INDICES FOR IDENTIFYING SEX PHEROMONES

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The gas-chromatographic retention indices of a number of unsaturated alcohols and their acetates and unsaturated epoxides on two phases of different polarities have been determined. The tabular results obtained have been used to determine the lengths of the chains and the functionalities of the sex pheromones of two species of moth *Mamestra brassicae* L. and *Mamestra oleracia* L.

In connection with the development of new methods of protecting plants that are harmless for the environment, particular interest is aroused by substances of natural origin — sex pheromones of insects, the use of which is regarded as extremely promising [1]. The isolation and determination of the structures of natural pheromones is associated with a number of difficulties due mainly to the small amounts of the substance contained in the insect glands (nanogram amounts). This leads to the necessity for using highly sensitive physical and physicochemical methods, and also their combinations with chemical identification.

*Deceased.

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