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Interrelation between the Composition of Liquid-Phase Ozonization Products and Structural Fragments of Various Genesis Coals

S. A. SEMENOVA, YU. F. PATRAKOV and M. V. BATINA

*Institute of Coal and Coal Chemistry, Siberian Branch of the Russian Academy of Sciences,
Ul. Rukavishnikova 21, Kemerovo 650610 (Russia)*

E-mail: chem@kemnet.ru

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Abstract

An influence of combustible minerals nature upon the yield and componential composition of their ozonization products in glacial acetic acid medium has been studied. It is established, that the basis of substances soluble in the reaction medium is formed by low-molecular water-soluble compounds. Benzenedicarbonic acids and their alkyl derivatives are revealed to prevail among water-soluble products of humus brown coal. The products of ozonolytic destruction of liptobiolite and sapropelite coal are presented mainly by aliphatic dicarbonic acids with the chain length corresponding to C_2-C_{10} .

Key words: liquid-phase ozonization, humus coals, sapropelites, liptobiolites

INTRODUCTION

A great number of works available from the literature is devoted to the obtaining of carbonic acids from coal raw material. The authors of [1–5] established that the main products of the oxidation of humolites and sapropelites represent the mixtures of aromatic acids (from brown and black coal) and aliphatic acids (from sapropels and combustible shales). Among the minerals of sapropelite origin, the products of oxidative destruction and the organic matter (OM) structure are most comprehensively studied for combustible shale [6, 7]. At the same time, the information concerning the oxidation of liptobiolite coal is scarcely available from the literature [5].

In order to perceive the nature of coals one should use methods promoting a selective “grinding” of the high-molecular structure of coal’s OM to yield rather low-molecular components those reflect the features of the initial OM structure. One of such methods based on a soft destructive influence upon coal’s OM is presented by ozonization. As against other oxidizing agents, ozone exhibits

a high selectivity and reactivity with respect to some types of bonds (for example, C=C bond) and heteroatoms (O, S). Moreover, ozonization does not require for using of catalysts as well as increased pressure and elevated temperatures [8].

The present work is aimed at the studies on the ozonization process and products composition for solid combustible minerals (SCM) of different genetic nature of humus, liptobiolite and sapropelite type coals at close chemical maturity stages.

EXPERIMENTAL

As a subject of inquiry we used the samples of brown coal (2B grade, the Barandat deposit, the Kemerovo Region), sapromixite coal (the Barzas deposit, the Kemerovo Region) and boghead coal (the Taymylyr deposit, Yakutia). According to genetic characteristics, these SCM belong to humus, liptobiolite (cuticular) [9], sapropelite types and represent natural concentrates (87–90 %) of vitrinite, liptinite and alginite groups, respectively.

TABLE 1

Characteristics of humus brown (HB) coal, the Barzas sapromixite (BS) coal and the Taymylyr boghead (TB) coal

| Samples | Petrographic composition*, % | | | | Technical analysis, % | | | Elemental composition, % daf | | | H/C | O/C | Functional composition, mg-eq/g | | | C _O ,** % daf | |
|---------|------------------------------|----|----|-----|-----------------------|----------------|------------------|------------------------------|------|-------|------|------|---------------------------------|------|------|--------------------------|--------------------|
| | Vt | I | L | Alg | W ^a | A ^d | V ^{daf} | C | H | O+N+S | | | COOH | OH | CO | O _{act} | O _{inact} |
| | HB | 90 | 10 | - | - | 8.0 | 8.8 | 48.0 | 69.4 | 4.6 | 26.0 | 0.79 | 0.25 | 1.19 | 383 | 1.52 | 11.38 |
| BS | 11 | - | 89 | - | 0.3 | 3.1 | 49.0 | 82.7 | 7.2 | 10.1 | 1.04 | 0.07 | 0.05 | 0.36 | 1.24 | 1.79 | 6.01 |
| TB | 13 | - | - | 87 | 1.2 | 3.5 | 79.1 | 82.3 | 9.7 | 8.0 | 1.41 | 0.07 | - | 0.15 | 0.11 | 0.32 | 5.48 |

* Vt, I, L, Alg – vitrinite, inertinite, liptinite and alginite, respectively.

** Oxygen content in the groups.

In order to exclude the influence of the inorganic part, the sample of the initial Barzas sapromixite coal (ash level $A^d = 34.6\%$) was exposed to demineralization by hydrochloric and hydrofluoric acids. The parameters of the samples are presented in Table 1.

Stepwise liquid-phase ozonization (the volume fraction of ozone being equal to 1.0–1.2%) was carried out at 20 °C in temperature-controlled rotating reactor. The weighed sample of coal amounted to 2 g. Glacial acetic acid (75 mL) was used as a solvent. The duration of one cycle was equal to 5 h. The products soluble with respect to acetic acid were separated into water-soluble (WS) and water-insoluble (WiS) substances.

The amount of oxygen-containing carbonyl groups was determined *via* the reaction with the hydroxylamine hydrochloride, the amount of carboxyl groups was determined using an acetate method, total acidity was determined by ion exchange with sodium hydroxide [10]. The content of oxygen in “active” groups (O_{act}) was determined through the summation of its percentage in the groups under identification; the amount of “inactive” oxygen (O_{inact}) was determined from the difference between the total content of oxygen and O_{act} value.

Diffuse reflection IR spectra were registered using a Bruker Tensor-27 FT-IR spectrometer. The chromatography/mass-spectrometry analysis was performed employing an Agilent 19091S-433 chromatograph within the range of 15–500 amu; an HP-5MS capillary column (5% diphenylsiloxane–95% dimethylsiloxane, 30 m × 0.25 mm i.d.; film thickness: 0.25 μm) was employed; helium was used as a carrier gas. The products to be chromatographed were preliminary methylated with diazomethane in diethyl ether medium [11].

RESULTS AND DISCUSSION

Despite of a close metamorphic (brown coal) stage, coal samples under investigation of humus, liptobiolite and sapropelite nature differ from each other in the structure of OM as well as in physicochemical properties. It could be caused by differences in the conditions of deposit formation (watering level, vital activity of bacteria, mineralogical composition, pH of medium, *etc.*) as well as in the composition of initial organic material (ground herbaceous and ligneous vegetation, protozoan algae, animal plankton). Most distinctly these differences are exhibited by changing the atomic ratio H/C: for brown coal and boghead coal this value amounts to 0.79 and 1.41, respectively (see Table 1). High H/C values for sapromixite coal and, especially, boghead coal (>1) as compared to those for humus coal indicate that the processes of their OM formation are close to the genesis of oil.

According to IR spectra of SCM (Fig. 1), the structure of boghead and sapromixite coal contains a relatively greater amount of aliphatic

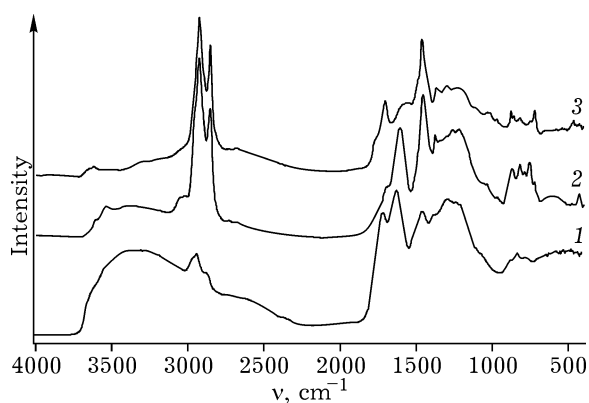


Fig. 1. IR spectra of humus brown coal (1), the Barzas sapromixite coal (2) and the Taymylyr boghead coal (3).

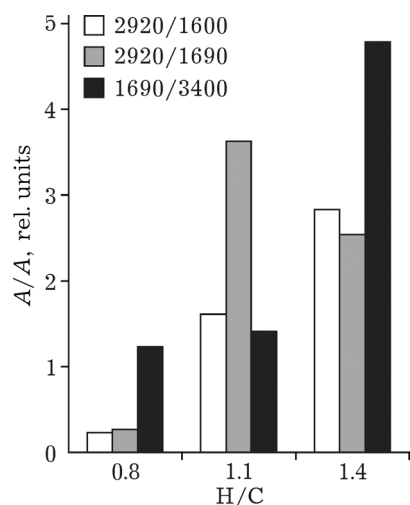


Fig. 2. Ratio between absorption band intensities for humus brown coal, the Barzas sapromixite coal and the Taymylyr boghead coal.

ic and(or) alicyclic fragments (CH_x , 2925, 2850, 1460, 1380 cm^{-1}) as compared to their content in the OM of brown coal. In this case aromatic fragments with a developed system of alkyl and functional substitution are, to all appearance, much more inherent in the structure of humus type coal, which is indicated by a set of low-intensity absorption bands for CH_{ar} groups at 3040 and 740–870 cm^{-1} coupled with a high intensity of the absorption band of C=C bonds at 1600 cm^{-1} .

The prevalence of reduction or oxidation-reduction processes at the stage of combustible minerals diagenesis determines the types of carbon-oxygen bonds and the forms of oxygen-containing groups therein. So, the presence of oxygen heteroatoms in the neutral form within ether "ligaments" (C–O, 1260 cm^{-1}), methoxy groups (CH_3 , 2850 cm^{-1} ; C–O, 1200–1275 cm^{-1}), cyclic aliphatic ketones (C=O, 1705 cm^{-1}), lactones (1740 cm^{-1}) and anhydrides (1780 cm^{-1}) is, to all appearance, more inherent in the structure of boghead coal. In OM of the Barzas coal there is, to all appearance, neutral oxygen within heterocycles prevailing (C=O, 1740 cm^{-1} ; C–O, 1260 cm^{-1}), whereas acidic O groups prevail in the structure within carboxyl groups (OH, 3200–3400, 2500–2800 cm^{-1} ; C=O, 1700–1750 cm^{-1} ; C–O, 1210–1440 cm^{-1}) and phenolic groups (OH, 3630 cm^{-1}).

The IR spectral parameters A_{2920}/A_{1600} and A_{2920}/A_{1690} reflecting the fraction of aliphatic fragments in coal OM with respect to aromatic

and oxygen-containing groups, respectively, are indirectly characterizing the differences between the coals under investigation in genetic features; they exhibit a regular increase with growing the atomic ratio H/C (Fig. 2). The tendencies for changing A_{1690}/A_{3400} parameter as a ratio between the absorption intensities of carbonyl groups C=O and OH groups of acid character (phenolic and phenolic and carboxylic ones) indicate that there is relative increase in the content of oxygen in neutral (quinoid, ketone, lactone) groups within coal OM with growing the atomic ratio $H_{\text{at}}/C_{\text{at}}$.

The kinetic curves for the accumulation of coal ozonization soluble products (Fig. 3) are s-shaped, which is inherent in chain radical oxidation processes for the majority of hydrocarbons where the initial stage is characterized by a slow development of reactions (the induction period), then there is the period of auto-accelerated development and the further degenerate chain branching [12]. The greatest rate of soluble products formation in acetic acid medium corresponds to humus brown coal, which could be caused by the presence of highly reactive aromatic C=C bonds ($k = 1 \cdot 10^2 - 1 \cdot 10^3 \text{ L}/(\text{mol} \cdot \text{s})$) and phe-

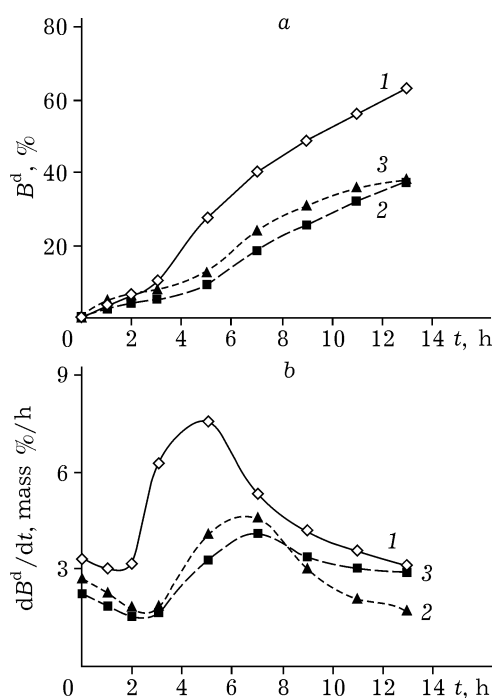


Fig. 3. Yield (a) and the formation rates (b) for coal ozonization products soluble in acetic acid depending on the process duration: 1 – humus brown coal, 2 – the Barzas sapromixite coal, 3 – the Taymylyr boghead coal.

nolic groups ($k = 1 \cdot 10^2 - 1 \cdot 10^4 \text{ L}/(\text{mol} \cdot \text{s})$) therein [8], as well as of naturally occurring polarized oxygen-containing fragments capable of dissolution.

Rather low yield of products for the coals of liptobiolite and sapropelite nature could also be caused by a lower content of C=C bonds therein (within aromatic structures and unsaturated "sites" of alkyl and cycloalkyl fragments) those are the most reactive with respect to ozone. Extreme changes in the content of functional O groups in OM of coals (Fig. 4) registered in the course of the process, to all appearance, could be connected with a gradual dissolution of the products oxidative coal destruction.

During 25 h of ozonization process (5 cycles), the amount of organic coal matter ranging from 52 to 92 mass % was converted into soluble compounds (Table 2). The amount of products formed increases in the series boghead coal–sapromixite coal–brown coal. In this case the total amount of soluble substances and the residual oxidized coal for all the samples is lower than 100 % (see Table 2). This negative balance with respect to the products of ozonization indicates that alongside with the processes of the synthesis of O groups in the surface layer of coal particles and soluble compounds, ozone also initiates destructive oxidation reactions connected with the removal of a part of OM in the form of volatile and gaseous substances.

The basis of products soluble in acetic acid is formed by rather low-molecular WS substances, in whose structure there are carboxyl groups prevailing (see Table 2). Water-insoluble products are characterized by a high con-

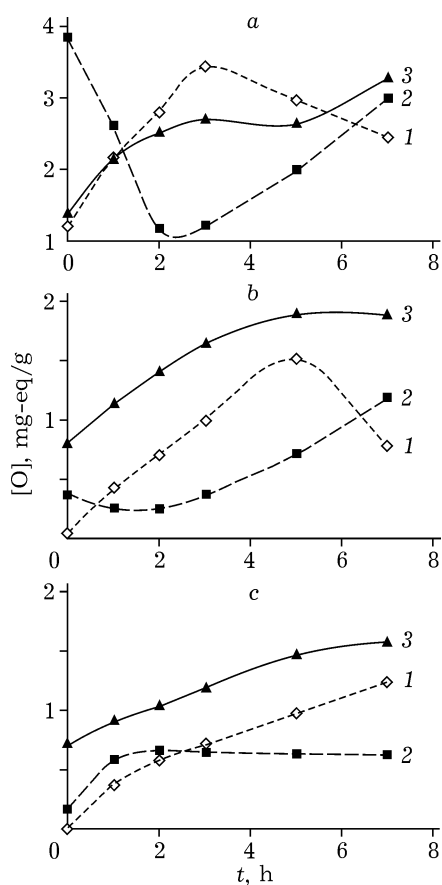


Fig. 4. Dynamics of content variation for carboxyl (1), hydroxyl (2) and carbonyl (3) groups during the ozonization of humus brown coal (a), the Barzas sapromixite coal (b) and the Taymylyr boghead coal (c) in acetic acid medium.

tent of carbon and by considerably lower O/C values; the fraction of "active" oxygen therein is 1.5–2.0 times lower than that for WS compounds.

IR spectra of WS products (Fig. 5) exhibit the maximal intensity of absorption bands cor-

TABLE 2

Parameters of water-soluble (WS) and water-insoluble (WiS) ozonization products for humus brown (HB) coal, the Barzas sapromixite (BS) coal and the Taymylyr boghead (TB) coal

| Samples | Product | Yield, % daf | | Elemental composition, % daf | | | H/C | O/C | Functional composition, mg-eq/g | | | C _o , % daf | | A ₂₉₂₀ /A ₁₆₀₀ |
|---------|---------|--------------|-------|------------------------------|-----|------|------|------|---------------------------------|------|------|------------------------|--------------------|--------------------------------------|
| | | Product | Total | C | H | O+N | | | COO | HOH | CO | O _{act} | O _{n/act} | |
| HB | WS | 73.5 | 94.4 | 52.5 | 3.9 | 43.6 | 0.89 | 0.62 | 8.91 | 1.97 | 5.06 | 35.71 | 7.89 | 0.36 |
| | WiS | 18.9 | | 61.3 | 4.8 | 33.9 | 0.94 | 0.41 | 5.42 | 1.48 | 4.29 | 23.14 | 10.76 | 0.46 |
| BS | WS | 47.4 | 92.5 | 51.2 | 4.4 | 44.4 | 1.03 | 0.65 | 9.27 | 0.05 | 4.84 | 33.62 | 10.78 | 0.84 |
| | WiS | 14.4 | | 65.0 | 6.2 | 28.8 | 1.14 | 0.33 | 5.23 | 0.02 | 3.90 | 19.89 | 8.91 | 2.16 |
| TB | WS | 44.4 | 97.3 | 54.8 | 5.5 | 39.7 | 1.20 | 0.54 | 7.60 | 0.69 | 3.72 | 28.40 | 11.30 | 0.53 |
| | WiS | 7.5 | | 63.7 | 7.5 | 28.8 | 1.41 | 0.34 | 2.86 | 1.08 | 4.08 | 14.14 | 14.66 | 1.76 |

*Including the total yield of WS, WiS products and of insoluble coal residue.

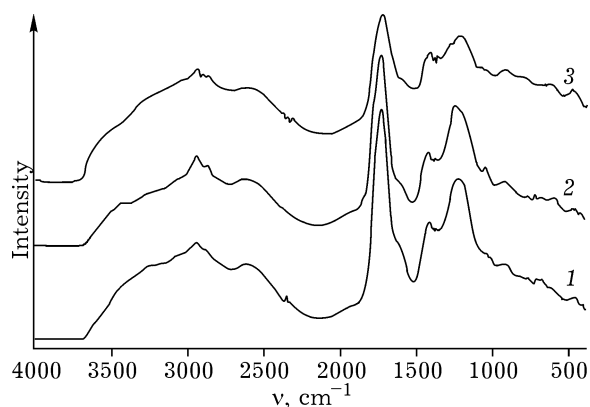


Fig. 5. IR spectra of water-soluble products obtained *via* ozonization in acetic acid medium from humus brown coal (1), the Barzas sapromixite coal (2) and the Taymylyr boghead coal (3).

responding to carbon-oxygen bonds of carbonic acids at $1700\text{--}1730\text{ cm}^{-1}$ and $1100\text{--}1300\text{ cm}^{-1}$ (C=O and C-O bonds vibration, respectively). Wide absorption bands in the wave number regions of $2500\text{--}3300$ and $880\text{--}960\text{ cm}^{-1}$ corresponding to OH groups connected through hydrogen bonds indicate that there are dimers of acids prevailing among the products.

Structural features of various genetic nature coals are exhibited by the structure of products obtained therefrom. So, higher values of the H/C ratio and A_{2920}/A_{1600} parameter are inherent in WS products of sapromixite and boghead coal ozonization, as against ozonization products of brown coal (see Table 2), which correlates with the mentioned parameters for initial coal (see Table 1, Fig. 2).

Table 3 demonstrates the results of chromatographic analysis performed for WS compounds etherified by diazomethane. The componential composition of ozonization products for the coals of sapropelite and liptobiolite nature is presented by a homologous series of saturated dicarbonic $C_2\text{--}C_{13}$ acids, chromatographed as their dimethyl ethers (see Table 3). The main part of these acids (70–80 rel. %) falls at short-chain acids ($<C_7$), whose formation could be connected with the oxidation of coals' OM cyclic part. Acids with a greater chain length, to all appearance, are formed resulting from the oxidation of straight-chain residues of polymeric unsaturated aliphatic acids, as well as of oxy- and ketoacids (initial biomaterial polycondensation products). The presence of a significant amount (27.9 %) of short-chained aliphatic monocarbonic oxyacids among

TABLE 3

Componential composition of esterified water-soluble ozonization products for humus brown (HB) coal, the Barzas sapromixite (BS) coal and the Taymylyr boghead (TB) coal

| Classes of compounds | Composition, rel. % | | |
|---|---------------------|------|------|
| | HB | BS | TB |
| Methyl esters: | | | |
| of aliphatic acids C_{16}, C_{18} | 0.9 | 0.5 | – |
| of aliphatic oxyacids C_3 | – | 27.9 | 1.0 |
| Oxylcanes $C_3\text{--}C_7$ | – | 7.4 | – |
| Ketoalkanes $C_5\text{--}C_9$ | – | – | 10.8 |
| Dimethyl esters of aliphatic dicarbonic acids: | | | |
| ethanedioic | 30.6 | 38.1 | 4.7 |
| propanedioic | – | – | 1.3 |
| butanedioic | – | 2.3 | 39.8 |
| pentanedioic | – | 4.6 | 10.6 |
| hexanedioic | 6.1 | 7.2 | 7.0 |
| heptanedioic | – | 3.2 | 6.2 |
| octanedioic | – | 2.5 | 4.9 |
| nonanedioic | – | 2.4 | 4.5 |
| decanedioic | – | 1.3 | 3.2 |
| undecanedioic | – | 1.0 | 2.3 |
| dodecanedioic | – | 0.6 | 1.7 |
| tridecanedioic | – | – | 1.2 |
| Dimethylphtalate | 14.1 | 1.4 | 0.8 |
| Dibutylphtalate | 28.6 | – | – |
| 2-Monoethylhehyl ester of 1,2-benzenedicarbonic acid | 13.9 | – | – |
| Unsaturated hydrocarbons C_{23} | 5.8 | – | – |

Note. Dash – not detected.

the products of the Barzas coal ozonization indicates that there is a considerable fraction of oximethylene fragments in the structure of sapromixite coal.

It should be noted that the componential composition of WS products obtained from the Barzas sapromixite coal ozonization in acetic acid medium, differs to a considerable extent from the composition of the products obtained *via* ozonizing the coal in chloroform [13]. In particular, in the case of ozonizing in non-polar solvent and subsequent extracting the products by acetone, the most abundant WS substances, alongside with dicarbonic aliphatic acids are presented by benzenedicarbonic acids as well as by steroid acids (with the hydrocarbonic skeleton of cyclopentahydrophenantrene type). The absence of similar compounds among

WS products of ozonization in acetic acid medium, as well as a high content of oxalic acid (38.1 %) could be caused, to all appearance, by the competition between selective ozonolytic reactions and much more destructive radical oxidation processes. Thus, one could assume that high ozone solubility in acetic acid and, as a consequence, an increase in ozone concentration in the reaction medium promote the oxidative destruction of coal OM fragments and soluble products to produce low-molecular aliphatic acids and carbon dioxide.

Among the products of humus brown coal ozonization, aliphatic acids are presented by monocarbonic ones such as palmitic acid (C₁₆) and stearic acid (C₁₈) those represent important components of phytoogenous fatty material, as well as by dicarbonic acids such as oxalic (C₂) and adipinic (C₆) acids, the destruction products of benzene and naphthene rings. Aromatic acids (orthophthalic acid and its alkylated derivatives) amount to about 60 % of identified substances, which indicates that aromatic structural units are prevailing in OM of humus coals at brown-coal maturity stage.

CONCLUSION

It is demonstrated that the method of liquid-phase ozonization represents an effective way to “disassembly” a high-molecular structure of organic coal matter to produce rather low-molecular components reflecting the features of the structure of initial organic substances. The ozonization in the medium of a low-polar solvent such as chloroform exhibits a greater selectivity.

Basing on the data concerning the products structure of boghead ozonization one can conclude that the structure of sapropelite is formed from linear and (or) branched saturated and unsaturated chains of extensive length those incorporate oxygen heteroatoms in oxo- and oxyforms and linking each other cyclic (to all appearance, two- and three-ringed) fragments of aromatic and hydroaromatic structure.

The analysis of ozonization products composition obtained from the Barzas sapromixite coal indicates an increase in the contribution of cyclic fragments with aromatic and (or) cyclohydroaromatic structure to the mentioned coal structure as compared to OM of sapropelite coal. Thus, oxygen heteroatoms, to all appearance, could be incorporated into polycyclic fragments mainly in keto and ether forms, too.

The vast majority of the ozonization products of humus brown coal is presented by benzenedicarbonic acids and oxalic acid formed as the result of aromatic structures destruction. The absence of multibasic benzenecarbonic acids indicates that there are aromatic units with a low condensation level substituted with O groups of mainly acidic character and aliphatic lateral “branches” of various lengths prevailing in OM of humus brown coals.

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