Autoxidation of thiols with cobalt(II) phthalocyanine-tetra(sodium sulfonate) attached to poly(vinylamine). Part 4. Influence of base density within the polymeric ligand

Citation for published version (APA):

Brouwer, W. M., Piet, P., & German, A. L. (1985). Autoxidation of thiols with cobalt(II) phthalocyanine-tetra(sodium sulfonate) attached to poly(vinylamine). Part 4. Influence of base density within the polymeric ligand. *Journal of Molecular Catalysis*, 29(3), 335-345. [https://doi.org/10.1016/0304-5102\(85\)80040-7](https://doi.org/10.1016/0304-5102(85)80040-7)

DOI:

[10.1016/0304-5102\(85\)80040-7](https://doi.org/10.1016/0304-5102(85)80040-7)

Document status and date:

Published: 01/01/1985

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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AUTOXIDATION OF THIOLS WITH COBALT(II) PHTHALOCYANINE-TETRA(SODIUM SULFONATE) ATTACHED TO POLY(VINYLAMINE) PART 4. INFLUENCE OF BASE DENSITY WITHIN THE POLYMERIC LIGAND

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(Received December 12, 1983; accepted February 13, 1984)

Summary

Water-soluble polymeric catalysts, consisting of cobalt(II) phthalocyanine-tetra(sodium sulfonate) coordinatively bound to poly(vinylamine-co-vinylalcohol), have been used in the oxidation by oxygen of 2-mercaptoethanol to its corresponding disulfide. An increase in the intrinsic activity of the catalytic sites was observed with increasing ethylamine (base group) content in the copolymers, while constant activation enthalpies indicated that the reaction mechanism remained unchanged.

From potentiometric titrations of the basic copolymers with hydrochloride and from catalytic activity measurements, it could be deduced that reaction rate varied linearly with the mole fraction of charged monomeric units in these copolymers.

A reaction scheme has been proposed, suggesting that the thiol anion is involved in the rate-limiting step.

The present polymeric catalyst and vitamin B₁₂ were found to show similarities in their oxidation behaviour toward thiols.

Introduction

During the last decade many papers concerning the oxidation of thiols have been published, as their great importance in oil-sweetening and biological processes became apparent. Many catalysts are known for the oxidation of thiols, and porphyrins and phthalocyanines in particular appeared to be useful catalysts [1, 2]. It has been shown that vitamin B₁₂ (Vit B₁₂), containing cobalt within a porphyrin-related structure, also catalyses the oxidation of thiols [3].

In our laboratory we have investigated cobalt(II) phthalocyanine-tetra(sodium sulfonate) (CoPc(NaSO₃)₄) attached to poly(vinylamine) (PVAm) as a polymeric catalyst in the oxidation of 2-mercaptoethanol

Fig. 1. Chemical structure of $\text{CoPc}(\text{NaSO}_3)_4$.

(RSH), and have observed a fifty-fold enhancement of reaction rate in comparison to polymer-free $\text{CoPc}(\text{NaSO}_3)_4$ (see Fig. 1) solutions. In the presence of 1,3-diaminopropane, which may be regarded as the monomeric analog of PVAm, the reaction rate also appeared to be much lower compared with the polymer-attached $\text{CoPc}(\text{NaSO}_3)_4$ system [4]. It has been shown from viscosity [5] and ESR measurements [6] that the metal centre of $\text{CoPc}(\text{NaSO}_3)_4$ is coordinated with five nitrogen atoms at most, when attached to PVAm. However, the importance of coulombic attraction between the four-fold negatively charged $\text{CoPc}(\text{SO}_3)_4^{4-}$ ion and the positively charged PVAm must not be ruled out, and may also contribute to the bonding.

So far, little is known of the detailed kinetics of thiol oxidation by polymer-bound $\text{CoPc}(\text{NaSO}_3)_4$. Only a few studies concerning porphyrins and phthalocyanines attached to polymers and polymeric sorbents have been published [7, 8].

In order to more fully understand the observed enhanced activity when using $\text{CoPc}(\text{NaSO}_3)_4$ attached to PVAm as a catalyst, the relations between catalytic activity on the one hand and pH, viscosity, reactant and catalyst concentrations, temperature and ionic strength on the other hand were investigated [9, 10]. A kinetic resemblance was found with the action of Vit B₁₂ derivatives in the oxidation of thiols. Recently we have shown that the enhanced basicity of low molecular weight PVAm in comparison to high molecular weight PVAm caused an increase in reaction rate. Local thiol anion concentration in the vicinity of the oxidation sites was assumed to be enhanced by the more basic character of low molecular weight PVAm [4].

We have now investigated the effect of local base strength by varying the amine group density within the polymer chain, by intercalation of non-charged spacer groups of variable length. For this purpose we have synthesised random copolymers of vinylamine and vinylalcohol (PVAm-co-VAl).

Materials and methods

Copolymers of vinylamine and vinylalcohol were synthesised by acid hydrolysis of poly(*N*-vinyl-*t*-butylcarbamate-co-vinylacetate) (PNVTBC-co-VAc) as described elsewhere [11]. Different mole fractions, α , of ethyleneamine in the copolymers could be obtained by varying the initial monomer feed ratio of *N*-vinyl-*t*-butylcarbamate and vinylacetate. The total conversion was controlled to not exceed 30%, in order to prevent heterogeneous copolymer formation. Values of α were obtained from elemental analysis (N content) of the pre-copolymers. The number-average molecular weight of these polymers was determined in toluene with a Hewlett Packard 502 high speed membrane osmometer operating at 37 °C.

In Table 1, monomer feed, copolymer composition data, number-average molecular weights and degree of polymerization (DP) have been listed. After being hydrolysed and eluted through an anion-exchange column (Amberlite IRA-401), stock solutions of copolymers were stored under nitrogen to prevent absorption of CO₂.

The molar *N*-group concentration (c_N) was determined by potentiometric titration with HCl (0.03 N) in 2 M NaCl. Catalytic activity measurements were carried out isobarically in an all-glass thermostatted Warburg apparatus, equipped with a mechanical glass stirrer. Oxygen consumption rates were measured with a digital flow meter apparatus.

The polymeric catalyst was prepared by adding an aqueous solution of CoPc(NaSO₃)₄ to a copolymer solution in water, resulting in a coordinatively-bound polymer complex. CoPc(NaSO₃)₄ concentration was 1.9×10^{-7} M under reaction conditions. The catalyst solution was degassed twice, saturated with oxygen, and the reaction was then started by adding the 2-mercap-

TABLE 1

Feed-copolymer compositional data, number-average molecular weight and degree of polymerization (DP) for the copolymerization of NVTBC with VAc in benzene at 60 °C

Sample	Mol fraction of NVTBC in feed	Mol fraction of NVTBC in copolymer (= α)	$10^{-3} \times \bar{M}_n$ (g mol ⁻¹)	DP
I	1.00	1.00	22	154
II	0.77	0.81	50	378
III	0.66	0.73	40	313
IV	0.56	0.63	40	328
V	0.45	0.56	33	280
VI	0.35	0.45	32	287
VII	0.26	0.39	27	364
VIII	0.13	0.20	69	708
IX	0.06	0.10	75	951
X ^a	—	—	72	1636

^aPoly(vinylalcohol) obtained from Koch Light Laboratories, U.K.

toethanol to the reaction vessel with a syringe. Initial reaction rates were calculated from the oxygen consumption during the first minute of reaction. Limitations of oxygen transport from the gas phase to the liquid were precluded by operating at a high stirring speed, *viz.* 2300 rpm, as described earlier [9].

Results and discussion

Previous investigations [9] have shown that the oxidation of 2-mercaptoethanol catalysed by PVAm-bound CoPc(NaSO₃)₄ can be described by Michaelis-Menten kinetics [12], indicating that in the reaction mechanism the rate-determining step takes place subsequent to enzyme-substrate complex formation:

where [E] = unbound enzyme, [ES] = enzyme-substrate complex and P = product. A plot of reciprocal reaction rate *versus* reciprocal substrate concentrations [S], a so-called Lineweaver-Burk plot, yields $(k_2[E_0])^{-1}$ as intercept, and extrapolation to $v^{-1} = 0$ yields $-K_m^{-1}$ as abscissa:

$$\frac{1}{v} = \frac{1}{k_2[E_0]} + \frac{K_m}{k_2[E_0]} \frac{1}{[S]} \quad (2)$$

$$\text{where } K_m = \frac{k_{-1} + k_2}{k_1} \left(\text{for } k_2 \ll k_{-1}: K_m \simeq \frac{1}{K_s} = \frac{k_{-1}}{k_1} \right) \text{ and}$$

[E₀] = total enzyme concentration, *i.e.* c_{CoPc(NaSO₃)₄}.

This type of kinetics has been observed with respect to both reactants, *i.e.* thiol and oxygen. At O₂ pressures above 0.1 MPa ($\simeq 5K_{m,O_2}$) the saturation plateau was reached as no further pressure dependence was observed [9].

For the present polymer VIII ($\alpha = 0.20$) we have verified the reaction rate to be independent of oxygen pressure around 0.1 MPa (at 0.06 MPa, reaction rate was 90% of that at 0.1 MPa). As a consequence, it may be assumed that at 0.1 MPa oxygen pressure the conversion of the thiol-CoPc(NaSO₃)₄ complex (see eqn. 2 in Scheme 1) rather than the catalyst reoxidation step (eqns. 3 and 4 in Scheme 1) will be rate-determining. All experiments reported in this paper, therefore, have been performed at 0.1 MPa oxygen pressure, while fairly high polymer concentrations have been used to avoid any effects of the molecular weight of the polymers on reaction rate [4].

For copolymers of different amine content (II, $\alpha = 0.81$, VIII, $\alpha = 0.20$ and IX, $\alpha = 0.10$) the apparent reaction constants k_2 and K_m have been

Fig. 2. Lineweaver-Burk plots for systems containing copolymers II ($\alpha = 0.81$, ■) and VIII ($\alpha = 0.20$, □). $c_{\text{N}} = 1.5 \times 10^{-3} \text{ M}$; $c_{\text{CoPc}(\text{NaSO}_3)_4} = 1.9 \times 10^{-7} \text{ M}$. pH = 7.8 (adjusted with 0.1 N NaOH).

Fig. 3. Arrhenius plots of k_2 . Copolymers as in Fig. 2; $c_{\text{RSH}} = 0.34 \text{ M}$; other concentrations and pH as given in Fig. 2. The value of k_2 has been approximated by:

$$\frac{v}{c_{\text{CoPc}(\text{NaSO}_3)_4}} \left(1 + \frac{K_m^{298}}{c_{\text{RSH}}} \right)$$

evaluated from Lineweaver-Burk plots, shown in Fig. 2 for II and VIII, according to eqn. 2.

In Fig. 3 Arrhenius plots are shown for copolymers II and VIII. It has been shown earlier [10] that ΔH_{m} is small in comparison to $\Delta H_2^\ddagger$, therefore the overall activation enthalpy virtually equals $\Delta H_2^\ddagger$ at high thiol concentrations, as can be derived from eqn. 2. Values of $\Delta H_2^\ddagger^{298}$, $\Delta S_2^\ddagger^{298}$, k_2^{298} and K_m^{298} are listed in Table 2, where it can be seen that a four-fold increase in amine group content in the polymer chain ($\alpha = 0.20$ to $\alpha = 0.81$) causes a two-fold increase in the intrinsic activity of the catalytic sites, indicated by the values of k_2 . The values of K_m remain unchanged and no significant dependence of $\Delta H_2^\ddagger$ on α is observed. As a result, it may be inferred that the reaction mechanism remains unaltered when the base density in the polymer chain is varied, and the apparent change in k_2 must be attributed to a change in apparent activation entropy $\Delta S_2^\ddagger$, including local concentrations (i.e. near the catalytic sites) of reactants involved in the rate-determining step.

TABLE 2

Effect of amine content in PVAm-co-VAl on some important reaction parameters at 298 K

α	$\Delta H_2^\ddagger$ (kJ mol ⁻¹)	$\Delta S_2^\ddagger$ (J mol ⁻¹ K ⁻¹)	$10^{-3} \times k_2$ (s ⁻¹)	K_m (mol dm ⁻³)
1.00	43 ± 4	-39 ± 10	4.5 ± 0.6	0.10 ± 0.01
0.81	39 ± 4	-53 ± 10	4.4 ± 0.5	0.09 ± 0.01
0.63	42 ± 4	-44 ± 10	3.7 ± 0.4	0.08 ± 0.01
0.39	36 ± 4	-68 ± 10	2.4 ± 0.4	0.08 ± 0.01
0.20	36 ± 4	-70 ± 10	1.9 ± 0.3	0.07 ± 0.01
0.10	41 ± 4	-57 ± 10	1.2 ± 0.2	0.08 ± 0.01

Unfortunately, $\Delta H_2^\ddagger$ cannot be determined with sufficient accuracy to avoid overlap of the error intervals of $\Delta S_2^\ddagger$. As a consequence, the changes in $\Delta S_2^\ddagger$, though plausible, cannot be evidenced conclusively.

K_m values cannot be interpreted unambiguously since K_m may depend both on the substrate-enzyme complex formation constant K_s and on the rate-determining constant k_2 (in particular if $k_2 \gg k_{-1}$); it seems, however, since K_m hardly alters when k_2 changes almost four-fold, that $k_2 < k_{-1}$ and no dramatic change in the apparent value of K_s is to be expected when the base density in the polymeric ligand is increased.

In order to find the relation between a polymeric parameter and the observed catalytic activity, reaction rates were measured at rather high thiol concentrations ($c_{\text{RSH}} = 0.3$ M, *i.e.* 3-4 K_m) for all copolymers. At these relatively high thiol concentrations, changes in reaction rate in fact reflect changes in k_2 . Ethyleneamine unit concentration was fixed at $c_N = 1.5$ mM (except for polymer X) and pH was maintained at 7.8.

Figure 4 (●) shows reaction rate as a function of α in the polymer chain. It is clearly seen that in the absence of basic amine groups ($\alpha = 0$) the reaction rate is virtually zero, and does not increase linearly with α but instead levels off with increasing values of α . It might be suggested that the sequence distribution of vinylamine units in the copolymer is related to the observed pattern of catalytic activity. This was investigated by calculating the number-average block length $\bar{l}$ [13] of ethyleneamine sequences in the copolymers with various α , using the monomer feed and copolymer composition data given in Table 1, and the reactivity ratios of NVTBC and VAc in benzene. The latter were determined as described elsewhere [11] and found to be $r_{\text{NVTBC}} = 1.12$ and $r_{\text{VAc}} = 0.46$ under the relevant conditions. As shown in Fig. 4 (□), the results reveal that the course of the catalytic activity *versus* α does not coincide with the dependence of $\bar{l}$ on α .

Another important polymeric parameter may be the degree of charge on the polymer, since this is expected mainly to determine the local concentration of thiolate ions by electrostatic attractions between RS^- and the positively-charged polymer chain.

Fig. 4. Various important parameters *versus* the mol fraction of ethyleneamine units in the polymeric ligand, α . (●) Reaction rate, v (expressed in converted thiol $\text{dm}^{-3} \text{s}^{-1}$), calculated from the oxygen consumption assuming that 1 mol O_2 reacts with 4 mol RSH to give H_2O and RSSR. $c_{\text{RSH}} = 0.28 \text{ M}$. Other concentrations and pH as given in Fig. 2. (□) Number average block length, $\bar{l}$, of ethyleneamine units in PVAm-co-VAl, calculated from the reactivity ratios of NVTBC and VAc and from the data in Table 1. (■) Mol fraction of charged monomeric units, $\alpha\sigma$, in PVAm-co-VAl derived from potentiometric titrations of the copolymers. $c_{\text{N}} = 0.01 \text{ M}$, pH = 7.8.

Fig. 5. pH *versus* the mol fraction of charged amine groups, σ , for $\alpha = 0.20$ (a); $\alpha = 0.45$ (b); $\alpha = 0.81$ (c) and $\alpha = 1.00$ (d). Curves have been derived from potentiometric titrations with HCl (0.03 N); $c_{\text{N}} = 0.01 \text{ M}$.

The pH as a function of the degree of protonation, σ , of the amine groups in the copolymers was determined by potentiometric titrations of all of the basic copolymer solutions ($c_{\text{N}} = 0.01 \text{ M}$) with HCl (0.03 N) at $22 \pm 1^\circ \text{C}$ in the absence of salt. The complete titrations were extended over a period of at least 20 min. The degree of protonation, σ , was calculated as follows:

$$\sigma = \frac{c_{\text{H}^+ \text{ added}} - c_{\text{H}^+ \text{ free}} + c_{\text{OH}^- \text{ free}}}{c_{\text{N}}}$$

Fig. 6. Reaction rate, v , versus the mol fraction of positively-charged monomeric units in the copolymers, $\alpha\sigma$, derived from Fig. 4.

where $c_{\text{H}^+ \text{ added}}$ is the molar proton concentration resulting from added HCl; $c_{\text{H}^+ \text{ free}}$ and $c_{\text{OH}^- \text{ free}}$ are the molar concentrations of free protons and hydroxyl ions measured in the titration vessel, respectively.

Figure 5 shows the pH versus σ at four values of α (for the sake of clarity not all curves have been drawn). Evidently the intrinsic basicity of the amine groups increases with decreasing α , which must be attributed to a decreased nearest neighbour interaction when the amine groups find themselves further apart in copolymers with a high vinylalcohol content [14]. In Fig. 4 ($\square$) this degree of separation of amine groups is shown by the occurrence of the asymptote $\bar{l} = 1$ when α adopts low values. Nonetheless, $\bar{l}$ is only a qualitative measure for the degree of separation, since amine group interactions are not exclusively of the nearest neighbour type.

It can easily be seen that the degree of charge on the copolymer chain (*i.e.* the mole fraction of charged monomeric units) at a certain pH value is represented by $\alpha\sigma$. In Fig. 4 ($\blacksquare$) $\alpha\sigma$ is plotted versus α at pH = 7.8, which is the pH during the catalytic activity measurements. The resemblance between the curves of $\alpha\sigma$ versus α , Fig. 4 ($\blacksquare$), and v versus α , Fig. 4 ($\bullet$) is striking. This conformity is confirmed by Fig. 6, where reaction rate is shown to vary linearly with polymer charge.

The polymeric catalyst in reaction solution, the latter containing a large excess of thiol with respect to amine groups, may be regarded as a concatenation of positively-charged rod-like segments, surrounded by a diffuse double layer of negatively-charged counter-ions, *i.e.* thiolate ions. Accordingly, the local thiolate ion concentration in the vicinity of the oxidation sites ($\text{CoPc}(\text{SO}_3)_4^{4-}$) is governed by the polymer charge.

In view of the observed linear increase of reaction rate with polymer charge, it seems therefore that the thiol anion is involved in the rate-determining step. On the other hand the complexation of $\text{CoPc}(\text{SO}_3)_4^{4-}$ to the

charged polymer chain may also depend on polymer charge. From ultrafiltration experiments with PVAm solutions containing $\text{CoPc}(\text{NaSO}_3)_4$ ($\text{Co/N} = 1:200$) it appeared, however, that blue $\text{CoPc}(\text{SO}_3)_4^{4-}$ could not be rinsed out. This behaviour appeared to be independent of the pH in the range $\text{pH} = 4 - 11$ and as a consequence independent of the polymer charge. This in contrast with the polymer-free $\text{CoPc}(\text{NaSO}_3)_4$ solutions, which passed the membrane easily.

From these observations it may be inferred that, due to the large excess of amine ligands with respect to Co as well as to the high charge of the $\text{CoPc}(\text{SO}_3)_4^{4-}$ ion, practically all $\text{CoPc}(\text{SO}_3)_4^{4-}$ will be present in the polymer domain under the relevant conditions. It does not seem that the rate dependence on the ethylamine mole fraction in the polymeric ligand can be explained from axial coordination effects, since the $\text{CoPc}(\text{NaSO}_3)_4$ in monomeric 1,3-diaminopropane solution appeared to be much less active than the polymer-attached $\text{CoPc}(\text{NaSO}_3)_4$.

Another polymeric property, related to polymer charge, is the polymer conformation. It may be assumed that the expansion of the polymer chain is enhanced by increasing chain charge. Conformation may affect catalytic activity, but neither transport limitations of reactants or products by coil diffusion nor a change of the reaction mechanism is to be expected in the light of the observed constancy of $\Delta H_2^\ddagger$ even at low α values.

According to the foregoing experimental observations, a preliminary reaction scheme may be proposed as shown in Scheme 1, eqns. 1 - 4. This scheme is consistent with the observed Michaelis-Menten kinetics in thiol and oxygen, although the rate-limiting step (eqn. 2 in Scheme 1) is first order in local thiolate ion concentration. It may be assumed that at neutral pH this local concentration is not affected very much by the thiol concentration in the bulk, and therefore Michaelis-Menten kinetics in thiol is still observed. Another interesting feature, following from the observed Michaelis-Menten kinetics with respect to thiol, is that obviously not thiolate but thiol interacts mainly with the metal centre (eqn. 1, Scheme 1). This is not so unexpected, since the electrostatic repulsion between the thiolate ion and the four-fold negatively-charged $\text{CoPc}(\text{SO}_3)_4^{4-}$ may hinder the approach of the metal centre by RS^- , although the negative charge of the $\text{CoPc}(\text{SO}_3)_4^{4-}$ will be shielded by the positive polymeric charge to some extent. Probably fast proton abstraction will be concomitant with or subsequent to complex formation. Following this train of thought it can be understood that the nucleophilic attack by RS^- according to eqn. 2 in Scheme 1 will be rate-determining.

Similar kinetic observations have been made by Nome and Fendler [15] in the investigation of the oxidation of L-cysteine by Vit $\text{B}_{12\text{a}}$. They were able to determine separately the apparent rate constants of reactions analogous to eqns. 1 and 2 in Scheme 1 pertaining to their system. They showed the equilibrium formation of a cysteine-Vit $\text{B}_{12\text{a}}$ complex prior to the electron transfer step, and the rate constant k_2 appeared to increase linearly with cysteine concentration at fixed pH, while k_2 increased expo-

Co_{red} = reduced $\text{CoPc}(\text{NaSO}_3)_4$

$\left\{ \begin{array}{c} \\ \\ \end{array} \right\}$ = polymer backbone

^aThe binding of $\text{CoPc}(\text{SO}_3)_4^{4-}$ to the polymer will be both coordinative and electrostatic in nature.

Scheme 1.

nentially with increasing pH, clearly indicating that the electron transfer step was first order in cysteinate ion.

The formation of H_2O_2 (eqn. 4 in Scheme 1) in the polymeric catalyst system at neutral pH has been shown earlier [16, 8], although it has not been proven to occur stoichiometrically with the formation of RSSR, probably due to further reaction of H_2O_2 with thiol. Recently Jacobsen [17] unequivocally has shown that in the aquocobinamid (a Vit B_{12} derivative) catalysed oxidation of various thiols H_2O_2 was formed stoichiometrically with RSSR. Obviously, in the oxidation of thiols to disulfides the polymeric catalyst and Vit B_{12} have many kinetic features in common, which may be partially attributed to the similarities in environment of the metal centres in both catalysts [18]. A further study concerning the polymeric effects in the polymeric catalysis of thiols is in progress.

Conclusions

In this investigation of the effect of base density in the polymeric ligand on the catalytic activity of a water-soluble polymeric catalyst in the oxidation of thiols, it has been shown that:

- there is no direct relation between base group block length and the intrinsic activity of the catalytic sites;
- the apparent rate-determining constant k_2 varies linearly with the charge on the polymer chain, while K_m is not significantly affected;
- within the experimental error the activation enthalpy $\Delta H_2^\ddagger$ does not change with the amine content in the copolymer, inferring that the reaction mechanism remains unaffected when base density within the polymeric ligand is varied;
- it becomes plausible that the thiol anion is involved in the rate-determining step (eqn. 2, Scheme 1) and that mainly RSH instead of RS^- is involved in the complex formation step (eqn. 1, Scheme 1);
- CoPc(NaSO₃)₄ attached to PVAm shows a kinetic resemblance with Vit B_{12a} in the oxidation of thiols to disulfides.

Acknowledgements

The authors are indebted to Prof. L. A. A. E. Sluyterman, Prof. R. Prins and Dr. T. P. M. Beelen for stimulating discussions and for a critical reading of the manuscript for this paper.

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