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Poly(Vinyl Chloride) Reactions with Sodium and Potassium Derivatives of Heteroaromatic and Aromatic NH- and SH-Acids in Aprotic Solvents

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Abstract—The observed featured and regularities of nucleophilic substitution of chlorine in poly(vinyl chloride) upon its reaction with sodium and potassium derivatives of pyrazole, 3,5-dimethylpyrazole, and 2-thiobenzimidazole, and with sodium thiophenolate have been understood in the frame of hard and soft acids and bases theory.

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Till nowadays, traditional methods of polymer synthesis are developing intensively, as evidenced by evolution of basic studies and technologies of preparation of new polymeric materials possessing a complex of valuable physicochemical and utilitarian properties. Firstly, this is applicable to functional modification of existing polymers, an important field of polymer materials science. This approach allows transformation of common industrial polymers into new materials with improved properties.

One of the cheapest (therefore, of specific practical interest) polymers is poly(vinyl chloride) PVC. More than 3000 of polymer materials are based on PVC.

The most widely applied technological recipe for PVC modification is its plastification with low-molecular mass organic compounds. However, there is another approach to modification of PVC properties: a chemical interaction with nucleophiles. PVC is known to interact with such agents as sodium and lithium azides [1], sodium 4-fluorothiophenolate [2], and sodium and potassium azole derivatives [3–5] via the mechanism of chlorine nucleophilic substitution. As this process is of high practical importance, it is necessary to extend the range of applied nucleophiles and to determine the optimal substitution conditions.

In this work we studied the nucleophilic substitution of PVC chlorine in its reactions with sodium and potassium salts of heteroaromatic and aromatic NH- and SH-acids, in particular, of pyrazole, 3,5-dimethylpyrazole, 2-thiobenzimidazole, and thiophenol.

The nucleophilic substitution of chlorine in PVC by the interaction with Na and K salts of pyrazole and 3,5-dimethylpyazole was performed in dimethylformamide (DMF), cyclohexanone (CH), and dimethylsulfoxide (DMSO), at 0–45°C (Table 1). The solvents were purified according to known procedures [6] prior to the reaction. The reaction running was evidenced by nitrogen presence in the final products. Above 0–2°C, the interaction of PVC with Na and K salts of pyrazole and 3,5-dimethylpyrazole led to insoluble products, and their color changed from yellow to black. The product composition as calculated from the chlorine content was different from that determined according to nitrogen fraction. This evidenced that PVC chlorine substitution was accompanied with dehydrochlorination. This was also reflected in the ^{13}C NMR spectra of the soluble final products, by the appearance of the ~HC=CH~ fragment signals (128.03–127.58 ppm), whereas in the IR spectra of both soluble and insoluble products the band at 1640 cm^{-1} appeared, characteristic of the polyvinylene units.

Run no.	Reagents ratio (molar)	Solvent	T, °C	Elemental analysis data, wt %				Yield[c], %	Solubility
				C	H	N	Cl[b]		
1	PVC:Na-PR = 1:1	DMF	0–2	42.69	4.68	1.47	50.68	24	Soluble
2	PVC:Na-PR = 1:1	DMF	10–12	45.42	5.17	1.84	44.36	27	Insoluble
3	PVC:Na-PR = 1:1	DMF	20–22	59.54	6.24	3.99	16.00	27	Insoluble
4	PVC:Na-PR = 1:1	DMF	40–45	47.46	6.45	1.36	38.08	29	Insoluble
5	PVC:Na-PR = 1:2	DMF	0–2	67.00	5.94	4.73	8.25	14	Insoluble
6	PVC:Na-DPR = 1:1	DMF	–10 to –15	41.03	5.90	0.85	53.76	35	Soluble
7	PVC:Na-DPR = 1:1	DMF	10–12	39.47	4.92	1.61	53.89	38	Insoluble
8	PVC:Na-DPR = 1:1	DMF	20–22	45.57	5.26	1.81	35.71	22	Insoluble
9	PVC:Na-DPR = 1:1	DMSO	20–22	48.34	5.59	2.04	36.49	23	Insoluble
10	PVC:Na-PR = 1:1	CH	40–45	47.12	5.70	1.29	42.54	20	Insoluble
11	PVC:Na-DPR = 1:1	CH	40–45	49.84	5.94	1.53	32.98	19	Insoluble
12	PVC:K-PR = 1:1	DMF	0–2	39.23	5.02	1.34	56.31	23	Soluble
13	PVC:K-DPR = 1:1	DMF	20–22	45.84	5.58	4.25	38.50	23.7	Insoluble
14	PVC:K-PR = 1:1	CH	20–22	43.16	5.46	0.26	49.53	23	Insoluble

[a] (PVC) poly(vinyl chloride), (PR) pyrazole, (DPR) 3,5-dimethylpyrazole, (CH) cyclohexane. [b] Residual Cl content in the modified PVC (initial PVC: 56.8 %). [c] Yield of modified PVC.

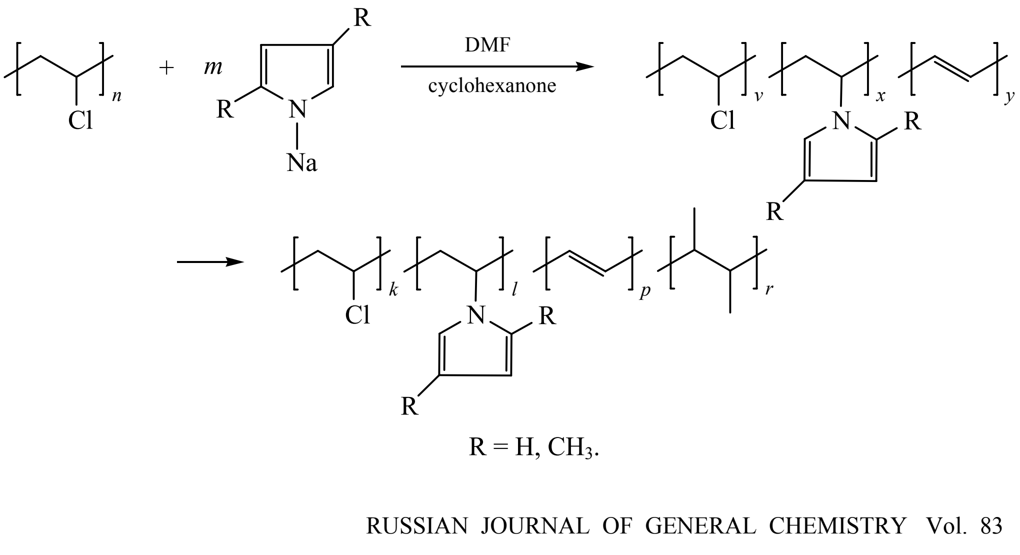
The chlorine substitution in PVC occurred according to the Scheme 1.

The formation of the internal double bonds in the macromolecule led to the possibility of the cross-linking and thus to the loss of solubility.

PVC interaction with sodium salt of 2-thiobenzimidazole in cyclohexanone gave only soluble products. On the contrary, in DMF medium both soluble and insoluble modified polymers were formed (Table 2).

According to Table 2 data, in the case of PVC interaction with sodium salt of 2-thiobenzimidazole the products were soluble even at high reaction temperature; thus, the chlorine substitution with 2-

Scheme 1.



R = H, CH_3.

Table 2. Poly(vinyl chloride) modification by sodium salt of 2-thiobenzimidazole (equimolar ratio of the polymer and the reagent)

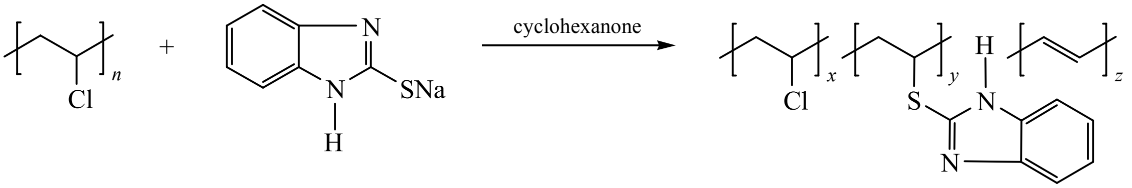
Run no.	Solvent	T, °C	Time, h	Elemental analysis data[a], wt %					Yield[c], %
				C	H	N	S	Cl[b]	
1	CH = Cyclohexanone	80	8	51.40	6.04	7.52	10.02	25.02	53
2	″	100	2	55.44	5.48	8.21	9.95	20.92	74
3	″	100	4	58.09	5.72	8.47	10.10	17.62	69
4	″	100	6	57.96	6.27	9.65	11.00	15.12	65
5	″	100	8	58.34	5.53	10.86	11.65	13.62	67
6	″	120	8	59.58	5.54	9.30	11.68	13.90	70
7	DMF	80	8	60.12	6.13	10.55	12.49	10.71	52

[a] Elemental analysis of the soluble product. [b] Residual Cl content in the modified PVC (initial PVC: 56.8 %). [c] Yield of modified PVC.

thiobenzimidazole group mainly occurred, and the dehydrochlorination reaction was less pronounced than in the case of pyrazole and 3,5-dimethylpyrazole salts. In the NMR spectra of the products characteristic broadened signals of CHCl and CH$_2$ of PVC groups protons (4.0–5.0 and 2.0–2.9 ppm, respectively [7]) appeared, as well as H^{4,7} and H^{5,6} of 2-thiobenzimidazole signals (δ_H = 7.6 and 7.1 ppm, respectively [7]) and broadened highly overlapping signals in the range of olefin protons resonance (5.0–6.7 ppm).

Double bonds were revealed in the polymer products by ^{13}C NMR spectra as well. Along with the vinyl chloride carbon signals of PVC (58.0–64.0 and 46.0–48.4 ppm for CHCl and CH$_2$, respectively) the spectra contained also broadened signals assigned to 2-thiobenzimidazole groups [δ_C, ppm: 110–118 (C^{4,7}), 122 and 126 (C^{5,6}), ~140 (C^{8,9}), and 142–150 (C^2)], and highly overlapping intensive signals in the range of 128–138 ppm corresponding to carbons of the olefin fragments HC=CH [8].

Thus, the following scheme reflected the substitution of chlorine in PVC at the reaction with 2-thiobenzimidazole sodium salt.



The products of PVC reaction with sodium thiophenolate were pale-yellow polymers, well soluble in DMF, DMSO, and CH (Table 3).

IR spectra of these reaction products contained the aromatic ring bands in the ranges of 3100–3020, 1600–1585, 1500–1400, and 900–670 cm^{-1}; and bands of PVC at 2970, 1333, 1254, and 1229 cm^{-1}, but no bands assigned to polyene fragments (1640 cm^{-1}) were observed.

In the ^{1}H NMR spectra, along with the signals at 1–4 ppm corresponding to the protons in the saturated polymer chains, the aromatic protons signal was observed at 7.27 ppm. In the ^{1}H NMR spectra of PVC modified with sodium thiophenolate at 85°C, the signals at 5.3–5.5 ppm, characteristic of the protons adjacent to internal double bonds, were absent; thus, under those conditions, dehydrochlorination reaction did not occur. However, in the ^{1}H NMR spectra of the same reaction performed at 155°C weak signals at 5.3–5.5 ppm appeared, pointing at internal double bonds formation.

Mechanism of nucleophilic substitution of PVC chlorine may be discussed in the frame of principle of hard and soft acids and bases [9, 10]. According to it, the hard bases are anions or molecules containing

Table 3. Interaction of poly(vinyl chloride) with sodium thiophenolate in cyclohexanone medium

Run no.	T, °C	Time, h	Elemental analysis data, wt.%		Degree of substitution, calculated from		Yield[b], %
			S	Cl	S	Cl[a]	
1	85	7	12.11	25.23	51.5	55.6	78
2	155	7	20.11	3.98	85.5	93.0	93

[a] Residual Cl content in the modified PVC (initial PVC: 56.8 %). [b] Yield of modified PVC.

electron donor atom with high electronegativity and low polarizability, with one or several lone electron pairs; the valence electrons are strongly held in place. Typical donor atoms in the hard bases are oxygen, nitrogen, fluorine, and chlorine. Soft bases, on the contrary, are electron donor molecules with low electronegativity and high polarizability; the valence electrons are weakly bound in them. Typical soft bases contain atoms of carbon, sulfur, and iodine.

The nucleophilic substitution reaction can proceed via monomolecular (S_N1) or bimolecular (S_N2) mechanism [11].

S_N1 chlorine substitution can be described by the following scheme.

$$RCl \rightarrow R^+ + Cl^-,$$

$$R^+ + Nu^- \rightarrow RNu.$$

If the stage of RCl dissociation occurs via S_N1 mechanism, the reaction is described by the first order kinetics equation. The reaction rate in this case is independent of the nature and the concentration of the nucleophile.

$$V = k[RCl].$$

If the formation of the bond with nucleophile and the leaving group elimination occur simultaneously (S_N2 mechanism), the reaction is a single-stage one.

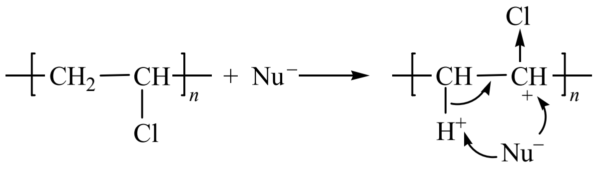
$$Nu^- + RCl \rightarrow [Nu^{\delta-}\cdots R\cdots Cl^{\delta-}] \rightarrow RNu + Cl^-.$$

This means that the reaction order is two: one with respect to the substrate and the nucleophile.

$$V = k[RCl][Nu^-].$$

The rate of such reaction strongly depends on the nucleophile nature and concentration.

Results of our study (Tables 1–3) showed that the degree of chlorine substitution in PVC was dependent on the nature of nucleophilic agent, and on its concentration; thus, all the studied reactions occurred via bimolecular mechanism and could be described by the following scheme.



The direction of the nucleophile attack depends mainly on the hardness or softness of the nucleophilic base. The proton is a hard acid, whereas carbon atom forming the R–Cl bond is a soft acid [9, 10]. Thus, softer nucleophile will attack the soft acid, the carbon atom; harder nucleophile will attack the hard acid, proton, predominantly.

Chlorine substitution is known to be often accompanied with HCl elimination [12, 13].

The pyrazole and 3,5-dimethylpyrazole are bases of intermediate softness, as lone electron pairs of nitrogen are delocalized along the π-system of the heterocycle [14]. The electron pairs orbitals of adjacent atoms are overlapping (α-effect); this decreases their basicity [15]. Basing on this considerations and taking into account the experimental results, sodium salts of pyrazole and 3,5-dimethylpyrazole attacked PVC molecule both via carbon of C–Cl bond (with the formation of substitution product), and via hydrogen of the adjacent C–H bond (leading to HCl elimination and the formation of NaCl and olefin group). The structure of the transition complex of S_N2 reaction was of bipyramidal shape, with 5 substituents at the reaction center [16]. Alkyl groups of the nucleophilic nitrogen led to stronger steric repulsion of the reagents in the transition complex, thus destabilizing the transition state with respect to the initial one, slowing down the reaction, and accelerating the rate of elimination, as in the latter process the transition state was less sterically strained. In the reactions of PVC with Na and K salts of pyrazole and 3,5-dimethylpyrazole, the nucleophile was relatively big, this favored the HCl elimination and the formation of internal double bonds in the polymer product.

The basicity of 3,5-dimethylpyrazole was higher than that of pyrazole, as acidity constant of the conjugated acid was lower (Table 4), due to the electron donor effect of the methyl groups. The difference in pK_a values of these nucleophiles (18 and 14, respectively) suggested that chlorine substitution in the case of PVC interaction with 3,5-dimethylpyrazole sodium salt should be faster than in the case of pyrazole Na salt. However, in the latter reaction more substituted product was formed, apparently due to the steric effect of methyl groups. For example, at 10–12 and 20–22°C PVC reaction with pyrazole sodium salt led to the substitution product containing 1.84% of nitrogen (Table 4, run no. 2) and 3.99% of nitrogen (Table 4, run no. 3), respectively, whereas under the similar conditions the products of PVC reaction with sodium salt of 3,5-dimethylpyrazole contained 1.61% and 1.81% of nitrogen, respectively (Table 4, runs nos. 7, 8).

Sodium salts of SH-acids (2-thiobenzimidazole and thiophenol), being soft bases, attacked mainly carbon atoms of C–Cl bonds in PVC (soft acid), thus forming the soluble substitution products (Table 2, run nos. 1–6, Table 3, runs nos. 1, 2).

It is known that the activation energy of elimination reaction is usually higher than that of the substitution process [11]. Thus, it could be assumed that heating should favor the elimination reaction, and temperature was expected to affect the E2/S_N2 products ratio. Indeed, the increase in the reaction temperature from 0°C to 20°C led to the increase in the nitrogen content in the product from 1.47% to 3.99% in the case of PVC interaction with sodium salt of pyrazole (Table 1, runs nos. 1–3). However, further increase in this reaction temperature to 40–45°C resulted in decreased nitrogen content, 1.36% (Table 1, run no. 4).

Similar trend was revealed in the case of PVC interaction with 2-thiobenzimidazole sodium salt: increasing the temperature from 80 to 100°C led the nitrogen content in the product to increase, from 7.52% to 10.86% (Table 2, runs nos. 1, 5), but further heating to 120°C resulted in slight decrease in the nitrogen content to 9.30% (Table 2, run no. 6). In the PVC reaction with Na salt of thiophenol at 85°C the only product was that of substitution reaction (Table 3, run no. 1). However, when the same reaction was performed at 155°C, polyvinylene units were found in the modified PVC (Table 3, run no. 2).

Table 4. Acidity constant of the nucleophilic center[a] [17, 18]

Nucleophilic center	pK_a
3,5-Dimethylpyrazole	18
Pyrazole	14
2-Thiobenzimidazole	8
~SC_6H_5	6.6

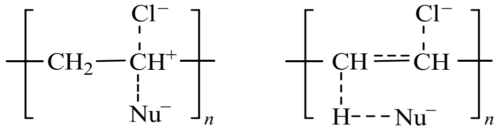
[a] DMF, 25°C.

The solvent nature affected significantly the rate and direction of the substitution and elimination reactions [11]. In this work, we only used aprotic solvents, in order to maintain the desired polymer solubility. Aprotic solvent did not form the specific hydrogen-bonded solvates with the nucleophilic agents; thus, the increase in the nucleophile basicity led always to increase in the nucleophilicity.

Pyrazole and 3,5-dimethylpyrazole were of higher basicity than 2-thiobenzimidazole and thiophenol, in line with the acidity constants of the respective conjugate acids (Table 4). This meant that pyrazole and 3,5-dimethylpyrazole were stronger nucleophiles than 2-thiobenzimidazole and thiophenol. Due to that, the latter pair of compounds was experimentally found to be less active in the bimolecular reactions of substitution and elimination. PVC reaction with sodium salts of pyrazole and 3,5-dimethylpyrazole occurred at lower temperature (Table 1), while in the cases of thiolated agents the reaction should have been run at 80–155°C (Tables 2, 3).

The solvent polarity also significantly affected the kinetics of substitution and elimination reactions. This was studied using the following nucleophiles: Na and K salts of pyrazole and 3,5-dimethylpyrazole, Na salt of 2-thiobenzimidazole, and of thiophenol; they could occur in the forms of free ions or ionic pairs in the bipolar solvents medium. The formation of ion pairs significantly decreased the nucleophile reactivity. On the contrary, the dissociation in the solvent of higher polarity (dielectric permeability) enhanced the nucleophile reactivity. PVC reaction with Na salt of 3,5-dimethylbenzimidazole in DMF and DMSO occurred similarly (Table 1, runs nos. 8 and 9). However, in the CH medium, other conditions being the same, the chlorine substitution degree noticeably decreased (Table 1, run no. 14 or Table 2, runs nos. 1 and 7).

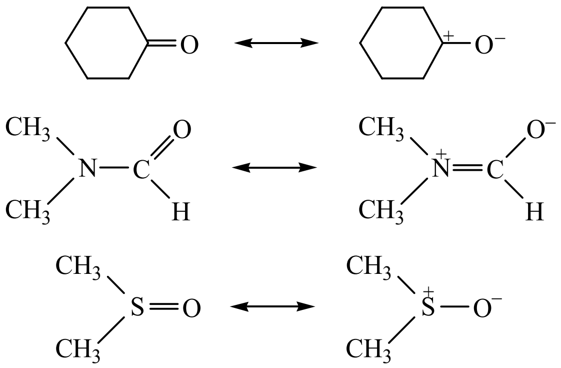
The charges distribution in the transition state of substitution S_N2 and elimination E2 reactions may be shown by the following scheme.



S_N2 E2

In the transition state of the elimination reaction, the negative charge delocalization was higher than that in the case of the substitution process. Thus, bipolar solvent containing softer acidic center led to better solvation of the nucleophile and favored the elimination reaction; on the contrary, the harder acidic center in the solvent favored the substitution reaction.

The resonance structures of the studied solvents were as follows.



In those structures, the positively charged carbon of CH was seemingly harder acidic center than those in DMF and DMSO. Many studies confirmed the acidity center hardness in the case of carbonyl compounds; nucleophilic addition to the C=O bond were subjected to the charge control [17]. The charge control meant that reactions of carbonyl compounds with nucleophilic reagents were faster when the positive charge at the carbonyl carbon and the negative charge at nucleophile were higher, in other words, then the Coulomb interactions between the reagents was stronger; this was a feature of hard reaction centers. This allowed concluding that the aprotic solvent nature affected the structure of the modified PVC. In the case of CH solvent (hard acidic center) the substitution reaction occurred predominantly (Table 2, runs nos. 1–6), the elimination being much slower. Elimination reaction in the PVC–2-thiobenzimidazole system was due to steric hindrance of the attack of the large nucleophile ion on the substrate (Table 2, runs nos. 1–6). In the system PVC–sodium thiophenolate–cyclohexanone at 85°C practically only substitution reaction occurred (Table 3, run no. 1), as the nucleophile volume was smaller, and the steric factor did not operate.

At the reaction of PVC with 2-thiobenzimidazole sodium salt in DMF medium (soft acidic center) the elimination reaction was accelerated, and both soluble and insoluble polymer products were formed (Table 2, run no. 7).

The results of this work demonstrated that the chlorine nucleophilic substitution was one of the most appealing reactions in the polymer chemistry, from both practical and theoretical points of interest.

EXPERIMENTAL

PVC prepared via emulsion polymerization was used, it was soluble in DMF, CH, and (partially) in DMSO. Its characteristics were as follows: Fikentscher constant K_F of 62–63, decomposition temperature of 120°C, and specific surface of 1.81 $cm^2 g^{-1}$.

Pyrazole, 3,5-dimethylpyrazole, 2-thiobenzimidazole, and thiophenol were purified commercial products. Pyrazole was sublimated in water-jet pump vacuum; 3,5-dimethylpyrazole was recrystallized from *n*-octane; 2-thiobenzimidazole was recrystallized from aqueous ethanol; and thiophenol was distilled.

The solutions viscosity was measured using the Ubbelohde capillary viscometer at 25°C.

Elemental analysis was performed with Thermo-Finnigan gas analyzer. IR spectra of the copolymers were recorded with Specord IR-75 spectrometer in the form of KBr tablets and in mulls in mineral oil; Bruker IFS-25 spectrometer was used as well.

^{13}C NMR spectra of the copolymers were recorded using VXR-500S Varian spectrometer (125.5 MHz) with the relaxation delay of 2.5 s, 90° impulse, in DMSO-d_6. Tris(acetylacetonate)chromium (0.02 mol/l) was used as relaxant. The relative integration error was of 3%. ^1H NMR spectra were recorded using DPX-400 Bruker spectrometer (frequency of 400.13 MHz) in C_6H_6-d_6 or DMSO-d_6.

Synthesis of Na and K salts of pyrazole, 3,5-dimethylpyrazole, 2-thiobenzimidazole, and thiophenol. 0.1 mol of NH or SH acid was dissolved in 100 ml of ethanol, and aqueous solution of equimolar amount of NaOH (or KOH) was added. The reaction mixture was incubated during 3 h at laboratory temperature. After the solvents removal, the salt was washed with ethanol and dried in the vacuum dessicator over P_2O_5. The salts purity was determined by potentiometric titration.

Poly(vinyl chloride) modification. Chlorine substitution reaction was run in the purified solvents. The respective salt was added in small portions to the 4 wt % solution of PVC at constant temperature (for details of reaction conditions, see Tables 1–3). The reaction products were isolated via dialysis or by precipitation in water, with subsequent filtration; washed with water, and dried.

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