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Electrosynthesis of diazene oxides under oxidation of nitramine anions at Pt in MeCN in the presence of nitrosobenzene

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The electrooxidation of anions of primary nitramine salts $RNNO_2^-M^+$ (R = Me, Et, methoxyfurazanyl; $M^+ = Bu_4N^+, Li^+, Na^+$) at a Pt anode in the presence of nitrosobenzene in divided and undivided cells was studied by potentio- and amperostatic electrolysis. Solutions of alkali metals and tetrabutylammonium salt in anhydrous MeCN were used as supporting electrolytes. Electrolysis can result in the formation of the corresponding diazene oxide, whose yield depends on the nature of the cation of the supporting electrolyte. In an undivided cell, the yield of diazene oxide increases owing to the regeneration of nitramine anions due to cathodic deprotonation of the nonionized form. The latter is formed by the stabilization of some radical intermediates by the elimination of hydrogen atoms from the components of the medium.

Key words: electrosynthesis of diazene oxides, nitramine anions, nitrosobenzene, electrooxidation, ionic association.

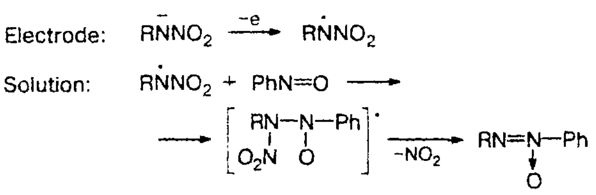
It has been found in the previous work[1] that the electrooxidation of nitramine anions at Pt in MeCN proceeds through the formation of the corresponding radicals, which are stabilized by the elimination of the hydrogen atoms from the components of the medium or undergo other transformations, including those to form azo derivatives. Based on these results, in this work, we performed the electrosynthesis of diazene oxides during the interaction of the indicated reactive species generated under the conditions of undivided electrolysis with nitrosobenzene as a radical trap.[2] In addition, based on the previously[3] established cathodic deprotonation of nitramines, we accomplished the "paired" process in the combined electrolysis of primary nitramines and nitrosobenzene in an undivided cell.

Results and Discussion

Nitrosobenzene (NB) is oxidized at the Pt electrode in MeCN at a more positive potential ($E_{1/2}$ = 1.4 V) than the oxidation potentials of methylnitramine (MNA), ethylnitramine (ENA), and 3-methoxy-4-nitraminofurazan (MNAF) anions, whose $E_{1/2}$ values are equal to 0.61, 0.63, and 0.95 V, respectively.

Therefore, we could expect that the electrooxidation of a mixture of the nitramine anion with nitrosobenzene under the conditions of undivided electrolysis at a controlled potential of at most 1.2 V occurs according to Scheme 1.

Scheme 1



Contrary to expectation, the process presented by Scheme 1 does not occur during the oxidative electrolysis of the MNA and ENA anions against the background of a 0.3 *N* solution of Bu_4NClO_4 in MeCN (Table 1, entries *1* and *4*). However, as for the *N*-alkylation of the electrogenerated nitramine anions,[3] diazene oxides were isolated from the reaction mixture in the case where the tetraalkylammonium salt in the composition of the supporting electrolyte was partially or completely replaced by the salt of an alkali metal (*cf.* entries *1, 2, 3* or *4, 5*).

These results agree with the concept concerning the effect of ion association on the dual reactivity of the anionic[3] and radical[1] intermediates, the products of the redox transformations of primary nitramines. It is known that the ambident properties of the nitramine anions[4] are manifested as the capability of these species to react in the form of *N*- and *O*-centered anions. We assume that the presence of alkali metal cations in a solution of the support favors the localization of the electron density on the amine nitrogen atom, and the probability of the formation of *N*-centered anions and radicals increases. The reactions involving precisely these species provide the desired synthetic result (*cf.* the previously published[1,3] data and the results presented above). By contrast, the presence of tetraalkylammonium cations that

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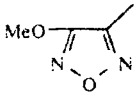
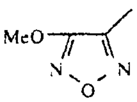
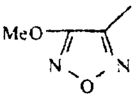
Table 1. Influence of the nature of the supporting electrolyte in oxidation potentio- (I) or amperostatic (II) electrolyses of salts of nitramines $RNNO_2^-M^+$ in the presence of NB on the yield of the corresponding diazene oxide

Entry[a]	R	Supporting electrolyte (concentration /mol L^{-1})	Yield of product (%)[b]	
			I[c]	II[d]
1	Et	Bu_4NClO_4 (0.3)	0.0	0.0
2	Et	Bu_4NClO_4 (0.2) $LiClO_4$ (0.5)	15.7	15.5
3	Et	$LiClO_4$ (0.5)	—	33.3
4	Me	Bu_4NClO_4 (0.3)	0.0	0.0
5	Me	$NaClO_4$ (0.1)	—	67.0
6		Bu_4NClO_4 (0.3)	22.5	24.1
7		$LiClO_4$ (0.5)	—	59.0
8[e]		Bu_4NClO_4 (0.3)	21.0	21.5

[a] Undivided cell, Pt anode, MeCN, quantity of electricity 1 $F\,mol^{-1}$.

[b] Calculated per loaded $RNNO_2^-M^+$.

[c] $E = 1.1$ V. [d] $j = 3$—5 mA cm^{-2}.

[e] Electrolysis in the absence of NB, the yield of 3,3′-dimethoxyazofurazan is presented.

are not prone to the formation of ion associates favor the formation of *O*-centered anions and radicals. The subsequent reactions of these species afford unstable products[5] that decompose on treatment of the reaction mixture.

Apparently, the replacement of the donating substituent at the nitrogen atom of the amino group by the withdrawing substituent changes the electron density distribution in the nitramine anions. In this case, the probability of the generation of the *N*-centered radical most likely increases when the nitramine anion is oxidized.[1] In fact, the paired electrolysis of NB and the MNAF anion, whose substituent at the nitrogen atom of the amino group possesses withdrawing rather than donating properties, showed (see entry *6*) that, unlike the ENA and MNA anions (entries *1* and *4*), the corresponding diazene oxide forms even when the tetraalkylammonium salt is used as the supporting electrolyte. Nevertheless, the yield of this diazene oxide increases when alkali metal perchlorate is added to the supporting electrolyte (*cf.* entries *6* and *7*). The nature of the metal itself affects the yield of diazene oxide rather than the replacement of the tetraalkylammonium cation by the alkali metal cation. Precisely this results, most likely, in the increase in the yield of the diazene oxide in entry *5* as compared to entry *3* during the electrolysis of the ENA and MNA anions, which are close in reactivity. However, we did not specially study this effect. Noteworthy is that the transition from the potentiostatic regime of electrolysis to the amperostatic regime at low current densities and under other equivalent conditions has almost no effect on the yield of the target products (entries *2* and *6*).

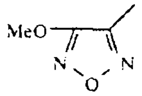
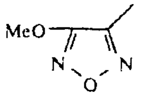
As we have shown previously,[1,3] the reaction mixture formed in the anodic space after electrolysis can contain up to 30% and more of the nonionized form of nitramine that formed due to the elimination of the hydrogen atom from the components of the medium by the radical intermediate.

The last circumstance made it possible to enhance the efficiency of the process under consideration if the nonionized nitramine, which is generated during electrolysis and inactive towards oxidation, is transformed into the anion. This possibility could be incarnated if a solution of the anolite formed in the experiments (see Table 1) is further treated under the conditions of undivided electrolysis. The nonionized nitramine, which is present in the anolite, undergoes deprotonation due to the cathodic reaction (as we have shown previously[3]). The results of the experiments confirmed this assumption. For example, a minor amount of the initial salt of the corresponding nitramine was added to the anolite formed after entries *2* and *6* (chosen as models) performed in the amperostatic regime. The obtained solutions were again subjected to amperostatic electrolysis but in an undivided cell, and 1—1.5 *F* of electricity per mole of the nitramine salt were additionally passed (the total concentration was taken into account). The results of the treatment of the reaction mixture after electrolysis showed that the yield of the corresponding diazene oxides increased (*cf.* the data of entries *2′* and *6′* in Table 2).

At the same time, azoxybenzene (15% calculated per loaded NB) was isolated from the reaction mixture in entry *2′* (see Table 2) along with 2-ethyl-1-phenyldiazene oxide. We have previously shown[1,3] that ENA ($E_{1/2} = -1.4$ V) is reduced at more negative potentials than MNAF ($E_{1/2} = -0.75$ V). This explains why in entry *2′* (unlike entry *6′*) the cathodic process, along with ENA reduction, is related to the partial reduction of NB to the azoxy derivative.

It has been found[1] that the potentiostatic electrolysis of the MNAF salt results in the formation of 3,3′-dimethoxyazofurazan in the anodic space of the divided cell. This agrees with the data of amperostatic electrolysis in the divided (entry *8*, see Table 1) and undivided cells (entry *8′*, see Table 2). Note that although the yield of 3,3′-dimethoxyazofurazan increases under the conditions of the undivided process, this increase is not so substantial as could be expected. An increase in the yield of the target product requires considerable (4 *F* per mole of the MNAF salt) expense

Table 2. Results of undivided electrolysis (*2'*, *6'*, and *8'*) of the reaction mixture obtained in entries *2*, *6*, and *8*, respectively (see Table 1)

Entry[a]	R	Preceding entry	$Q_{add}{}^{b}/F\,mol^{-1}$	$j/mA\,cm^{-2}$	Product	Yield of product (%)[c]
2'	Et	*2*	1.0	5.0	Diazene oxide	19.0
6'		*6*	1.5	3.5	Diazene oxide	62.0
8'[d]		*8*	4.0	3.6	3,3'-Dimethoxyazofurazan	40.5

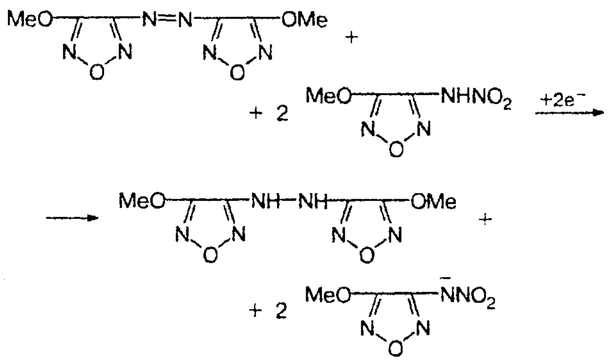
[a] The amount of the added $RNNO_2{}^-M^+$ was 10% in all experiments.

[b] The quantity of additionally passed electricity.

[c] Calculated per total concentration of the loaded $RNNO_2{}^-M^+$. [d] Electrolysis in the absence of NB.

of electricity. This is due to the fact that the reduction of the nonionized form of MNAF ($E_{1/2}$ = −0.75 V) is somewhat more difficult than that of 3,3'-dimethoxyazofurazan (the reversible one-electron wave[1] with $E_{1/2}$ = −0.70 V). Therefore, it is probable that during electrolysis (entry *8'*) the reduced form of 3,3'-dimethoxyazofurazan acts as an electrogenerated base with respect to the nonionized form of MNAF (the electrochemical version of the Wittig reaction in the presence of azobenzene[6] is a classical example of this process) and is partially consumed, transforming into the hydrazo derivative according to Scheme 2.

Scheme 2



The results presented above agree with the conclusions of the previous work[1] and indicate that the oxidation of the nitramine anions affords the radical intermediate whose reaction with NB present in the reaction mixture gives the corresponding diazene oxides. The yield of the diazene oxides substantially depends on the nature of the cation of the supporting electrolyte, which is due to the influence of ionic association on the reactivity of the nitramine anions and radicals exhibiting ambident character. According to the data of ^{1}H NMR spectroscopy, the reaction of the ENA radical with NB affords one isomer, whereas in the case of MNA, a mixture of isomers in a ratio of 1 : 2.7 is formed (see Experimental).

The observed[1] interaction of the nitramine radicals with the medium to eliminate the hydrogen atom (formation of nonionized nitramine) is confirmed by the results of electrolysis in an undivided cell: the regeneration of the nitramine anions due to the cathodic deprotonation of their nonionized form increases the yield of the corresponding diazene oxides. It is also noteworthy that NB is a very efficient trap of nitramine radicals because 3,3'-dimethoxyazofurazan, a probable product of the dimerization of nitrene species[1] generated by the fragmentation of the corresponding radical intermediate, is not formed in the presence of NB.

Experimental

^{1}H NMR spectra were recorded on a Bruker WM-250 instrument, mass spectra were obtained on a Varian MAT-311A instrument (EI, 70 eV), and IR spectra were recorded on a Specord IR-75 instrument. The reactions were monitored by TLC on Silufol UV-254 plates (benzene as eluent).

Preparative electrolysis of nitramine anions in the presence of NB (ratio ~1 : 2) was carried out in a thermostatted (25.0 °C) 130-mL glass cell with cathodic and anodic spaces divided with a porous glass filter or in an undivided cell with the same volume. For electrolysis in the potentiostatic regime, a P-5827M potentiostat was used, and a B5-49 current source was used for amperostatic measurements. A Pt plate (surface area 28 or 18 cm^2) served as anode, a Pt plate (surface area 8 cm^2) served as cathode, and Ag/0.1 *N* $AgNO_3$ was the reference electrode. The supporting electrolytes were 0.3—0.5 *N* solutions of Bu_4N^+, Na^+, and Li^+ perchlorates in anhydrous MeCN. Acetonitrile was dehydrated by fivefold distillation over P_2O_5 followed by distillation with calcined K_2CO_3.

Before electrolysis, working solutions were deaerated using argon. After electrolysis, solutions were treated by a standard procedure.

Treatment of solutions after electrolysis (general procedure). After electrolysis, diethyl ether (500 mL) was added to the reaction mixture, and the resulting mixture was washed with water (4×100 mL). The organic phase was separated and dried with anhydrous $MgSO_4$, and the solvent was distilled off on a rotary evaporator *in vacuo* without heating. The residue was separated on a chromatographic column with silica gel L (40/100 μm) using benzene as the eluent.

MNA and ENA specimens were synthesized by previously described[7,8] procedures. Tetrabutylammonium and sodium salts of these nitramines were obtained by the following procedure: diethyl ether was added to a methanol solution of KOH until a slight turbidity, and then the calculated amount of MNA (ENA) was added. The precipitated potassium salt of MNA (ENA) was filtered off and washed with a methanol—diethyl ether (3 : 1) mixture. An equimolar amount of $NaClO_4$ or Bu_4NClO_4 dissolved in methanol was added to the prepared potassium salts of nitramines. The mixture was stirred, and $KClO_4$ that precipitated was filtered off. After the evaporation of the methanol solution, Na^+ or Bu_4N^+ salt of MNA (ENA) was obtained and further used in the reaction without additional purification. The synthesis of the tetrabutylammonium salt of MNAF has been described previously.[1]

Electrosynthesis of diazene oxides in a divided cell (see Table 1). Entry *1.* A mixture of tetrabutylammonium salt of ENA (14 mmol) and nitrosobenzene (28 mmol) was dissolved in a 0.3 *N* solution (100 mL) of Bu_4NClO_4 in anhydrous MeCN and placed into the anodic space of the divided cell. During electrolysis with a controlled potential (E = 1.1 V), 1 *F* of electricity per mole of ENA salt was passed. After the end of electrolysis, the reaction mixture was treated by a standard procedure (see above). However, after the separation of the electrolysis products on a chromatographic column, the desired 2-ethyl-1-phenyldiazene oxide was absent (according to the data of elemental analysis, IR spectroscopy, and ^1H NMR) (*cf.* entry *2*).

Entry *2.* A mixture of the tetrabutylammonium salt of ENA (14 mmol) and nitrosobenzene (28 mmol) was dissolved in anhydrous MeCN (100 mL) and placed into the anodic space of an undivided cell. Electrolysis was carried out in the potentiostatic regime (see entry *1*), and Bu_4NClO_4 and $LiClO_4$ were preliminarily added to the reaction mixture to reach concentrations of 0.2 and 0.5 mol L^{-1}, respectively. The resulting solution was treated by the general procedure and separated on a chromatographic column (R_f = 0.32). 2-Ethyl-1-phenyldiazene oxide (0.33 g) was obtained (15.7% calculated per loaded ENA salt). Found (%): C, 63.82; H, 6.49; N, 19.02. $C_8H_{10}N_2O$. Calculated (%): C, 63.98; H, 6.71; N, 18.66. IR (film on NaCl), ν/cm^{-1}: 3080 w, 3030 w, 2980 w, 2940 w, 2910 w, 2880 w, 1530 w, 1480 m, 1465 m, 1455 m, 1425 m, 1385 w, 1340 m, 1320 m, 1310 s, 1175 w, 1115 w, 1100 w, 1070 w, 1040 w, 1020 w, 930 w, 870 w, 775 s, 690 s, 680 s. ^1H NMR (acetone-d_6), δ: 1.36 (t, 3 H, CH_3); 3.66 (q, 2 H, CH_2); 7.54 (m, CH arom.); 8.17 (d, CH arom.). MS, *m/z*: 150 $[M]^+$.

In entry *2* in the amperostatic regime (j = 5.5 mA cm^{-2}) and after treatment of the reaction mixture using a similar scheme, 0.32 g of 2-ethyl-1-phenyldiazene oxide were isolated (15.2% calculated per loaded ENA salt).

Entry *3.* Potassium salt of ENA (14 mmol) was added to an 0.65 *N* solution (100 mL) of $LiClO_4$ in anhydrous MeCN, and the precipitate of $KClO_4$ was filtered off. Nitrosobenzene (28 mmol) was added to the remaining ~0.5 *N* solution of $LiClO_4$ (100 mL) containing the lithium salt of ENA (14 mmol). The resulting mixture was placed into the anodic space of an electrolyzer. Electrolysis was performed in the amperostatic regime (j = 5.5 mA cm^{-2}), passing 1 *F* of electricity per mole of ENA salt. The reaction mixture was treated and analyzed as in entry *2.* 2-Ethyl-1-phenyldiazene oxide (0.7 g) was isolated (33.3% calculated per loaded ENA salt).

Entry *4.* The reaction mixture was prepared, electrolyzed, and analyzed in the same manner as in entry *1*, but instead of 14 mmoles of the tetrabutylammonium salt of ENA the same amount of the tetrabutylammonium salt of MNA was added. 2-Methyl-phenyldiazene oxide was not observed in the electrolysis products (*cf.* entry *5*).

Entry *5.* The sodium salt of MNA (14 mmol) was added to an 0.1 *N* $NaClO_4$ solution (100 mL) in anhydrous MeCN. The obtained reaction mixture was placed in the anodic space of the electrolyzer. Electrolysis was carried out in the amperometric regime (j = 5.5 mA cm^{-2}), passing 1 *F* of electricity per mole of MNA salt. The reaction mixture was evaporated, and the residue was extracted with diethyl ether. 2-Methyl-1-phenyldiazene oxide (1.28 g) was obtained (67% calculated per loaded MNA salt), b.p. 46.5 °C (2.5 Torr). Found (%): C, 61.81; H, 6.04; N, 20.35. $C_7H_8N_2O$. Calculated (%): C, 61.75; H, 5.97; N, 20.58. IR (film on KBr), ν/cm^{-1}: 3080 w, 3030 w, 2980 w, 2940 w, 2930 w, 2860 w, 1605 w, 1495 s, 1452 m, 1425 m, 1320 w, 1308 w, 1160 w, 1108 w, 1070 w, 1025 w, 926 w, 775 s, 688 s. ^1H NMR (acetone-d_6), δ: 3.1 (s, 3 H, CH_3); 3.39 (s, 3 H, CH_3); 7.6—7.73 (m, CH arom.); 7.77—7.88 (m, CH arom.); 8.2—8.3 (m, CH arom.). The intensities of the signals from CH_3 in the regions of δ 3.1 and 3.39 are related as 2.7 : 1, which indicates a mixture of the isomers. MS, *m/z*: 136 $[M]^+$.

Entry *6.* A mixture of the tetrabutylammonium salt of MNAF (10 mmol) and nitrosobenzene (19 mmol) were dissolved in an 0.3 *N* solution (90 mL) of Bu_4NClO_4 in anhydrous MeCN and placed into the anodic space of the divided cell. During electrolysis with a controlled potential (E = 1.2 V), 1 *F* of electricity per mole of MNAF salt was passed. The resulting solution was treated by the general procedure and separated on a chromatographic column (R_f = 0.49). 2-(3-Methoxyfurazan-4-yl)-1-phenyldiazene oxide (0.5 g) was obtained (22.5% calculated per loaded MNAF salt). Found (%): C, 49.56; H, 3.68; N, 25.47. $C_9H_8N_4O_3$. Calculated (%): C, 49.09; H, 3.66; N, 25.45. IR (KBr), ν/cm^{-1}: 3552 s, 3500 s, 3416 s, 1645 w, 1620 m, 1600 s, 1485 s, 1445 m, 1430 s, 1340 s, 1320 m, 1270 m, 1205 w, 1165 w, 1110 w, 1070 w, 1030 m, 990 s, 930 m, 865 w, 855 m, 790 s, 750 w, 690 s, 675 w, 645 m. ^1H NMR (acetone-d_6), δ: 4.18 (s, 3 H, CH_3); 7.75 (m, CH arom.); 8.36 (m, CH arom.). MS, *m/z*: 220 $[M]^+$.

When the experiment was carried out in the amperostatic regime (j = 3.6 mA cm^{-2}) and the reaction mixture was treated by a similar scheme, we isolated 0.53 g of 2-(3-methoxyfurazan-4-yl)-1-phenyldiazene oxide (24.1% calculated per loaded MNAF salt).

Entry *7.* A solution of $LiClO_4$ in anhydrous MeCN (90 mL, 0.5 *N*) containing the lithium salt of MNAF (10 mmol) and NB (19 mmol) (prepared according to the scheme described in entry *3*) was placed into the anodic space of the divided cell. Electrolysis was carried out in the amperostatic regime (j = 3.6 mA cm^{-2}), passing 1.1 *F* per mole of MNAF salt. The reaction mixture was treated and analyzed as in entry *6.* 2-(3-Methoxyfurazan-4-yl)-1-phenyldiazene oxide (1.3 g) was isolated (59.0% calculated per loaded MNAF salt).

Entry *8.* Tetrabutylammonium salt of MNAF (8.62 mmol) in an 0.3 *N* solution (85 mL) of Bu_4NClO_4 in anhydrous MeCN containing 17 mmoles of NB was placed into the anodic space of the divided cell. Electrolysis was carried out in the amperostatic regime (j = 3.6 mA cm^{-2}), passing 1.1 *F* per mole of MNAF salt, after which the reaction mixture was treated by the general procedure. 3,3′-Dimethoxyazofurazan (0.21 g) was isolated (21.5%

calculated per loaded MNAF salt). According to the data of TLC, IR spectrometry, and ^{1}H NMR, the sample is identical to authentic 3,3′-dimethoxyazofurazan.[7] The potentiostatic electrolysis of the MNAP salt has been described in the previous work.[1]

Electrosynthesis of diazene oxides in an undivided cell (see Table 2). Entry *2′*. Tetrabutylammonium salt of ENA (1.5 mmol) was added to the anolite after electrolysis (entry *2*, see above). The obtained mixture was placed into an undivided cell and subjected to electrolysis in the amperostatic regime with the anodic current density j = 5.5 mA cm^{-2}, passing 1 F per mole of ENA salt (taking into account the total load of the salt). The resulting solution was treated and analyzed as in entry *2*. 2-Ethyl-1-phenyldiazene oxide (0.44 g) (18.9% calculated per loaded ENA salt) and azoxybenzene (0.45 g) (15% calculated per starting NB) were obtained.

Entry *6′*. After electrolysis, the tetrabutylammonium salt of MNAF (1 mmol) was added to the anolite (entry *6*, see above). The resulting mixture was placed in an undivided cell and subjected to electrolysis in the amperostatic regime with the anodic current density j = 3.5 mA cm^{-2}, passing 1.5 F per mole of MNAF salt (taking into account the total load of the salt). The resulting solution was treated and analyzed as in entry *6*. 2-(3-Methoxyfurazanyl-4)-1-phenyldiazene oxide (1.52 g) was obtained (62.8% calculated per loaded MNAF salt).

Entry *8′*. Tetrabutylammonium salt of MNAF (0.86 mmol) was added to the anolite after electrolysis (entry *8*, see above). The obtained mixture was placed into an undivided cell and subjected to electrolysis in the amperostatic regime with the anodic current density j = 3.6 mA cm^{-2}, passing 4.0 F per mole of MNAF salt. The resulting solution was treated by the general procedure. 3,3′-Dimethoxyazofurazan (0.434 g) was obtained (40.5% calculated per loaded MNAF salt).

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