REACTION SEQUENCE IN HYDROGENATION OF UNSATURATED NITROXYL RADICALS ON GROUP VIII METALS

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Reactions that do not involve the free valence have great importance in the transformations of the derivatives of nitroxyl radicals in that they open up paths for the synthesis of new radicals [1]. However, the selective reduction of the unsaturated groups in such radicals is a complex problem, since trivial reaction involving the unpaired electron can easily take place in this case. In this connection it seemed interesting to study the catalytic hydrogenation of some unsaturated stable nitroxyl radicals, and specifically the esters of the vinylbenzoic, acrylic, and methacrylic acids



The reaction was run in alcohol solution in the presence of Raney Ni, the Pt-, Pd- or Rh-blacks, or the homogeneous catalyst, the RhCl(PPh_3)₃ complex.

The transformations that were observed in the catalytic hydrogenation of radical (I) are depicted in the following scheme



The realized reaction path is determined by the nature of the catalyst. On Raney Ni the process proceeds by the consecutive scheme: $(I) \rightarrow (IV) \rightarrow (VI) \rightarrow (VII)$. The radical center is reduced in the first step: the unsaturated substituted hydroxylamine (IV) is obtained in high yield. The olefinic bond is hydrogenated in the second step, and then the formed saturated hydroxylamine (VI) is reduced to the corresponding amine (VII (Fig. 1a).

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Fig. 1. Change in catalyzate composition when radical (I) is hydrogenated on the catalysts: a) Ni; b) Pt; c) Pd. 1) Radical (I); 2) substituted hydroxylamine (IV); 3) radical (V); 4) substituted hydroxylamine (VI).

TABLE 1. Ratio of Hydrogenation Rate Constants $k_{0}C=C/k_{0}NO$.

Catalyst	Radical	Individual	Mixture of			
	(I)	(VIII and IX)	(VIII and IX)			
SkeletalNi	$\begin{array}{c} 1,0\\ 0,22\\ 20,0\\ 2,0 \end{array}$	0,8	1,1			
Pt-black		0,15	0,17			
Pd-black		15,0	23,0			
Rh-black		2,0	2,1			

The same sequence of reactions is retained when the hydrogenation is run in the presence of Pt-black: the radical center is reduced first, and then the vinyl group (Fig. 1b): $(I) \rightarrow (IV) \rightarrow (VI)$. It should be mentioned that on Pt, in contrast to Ni, in harmony with the literature data, the substituted hydroxylamine is not reduced to the amine for the nitroxyl radicals that do not contain the C=C bond [2].

The reaction proceeds most interestingly on the Pd catalyst: (I) \rightarrow (V) \rightarrow (VI). The vinyl group is selectively

reduced in the first step without involving the radical center and a new radical (V) is formed (see Fig. 1c).

The nitroxyl group and the radical center are reduced simultaneously on Rh-black

$$(I) \qquad (V) \qquad (V)$$

The observed reaction sequence for the reduction of the vinyl and nitroxyl groups of radical (I) on Ni and Pt cannot be explained if only the ratio of the hydrogenation rates of these groups is taken into account. Actually, as can be seen from the kinetic curves (Fig. 2), on the Ni catalyst the reduction of the double bond proceeds at a faster rate than the saturation of the radical center. For the Pt catalyst the rates of these steps are close.

To estimate the reactivity of the nitroxyl and vinyl groups we studied the hydrogenation rates of methyl p-vinylbenzoate (VIII) and the stable radical 2,2,6,6-tetramethyl-1-oxyl-4-hydroxypiperidine (IX), which represent the fragments of radical (I). The reduction of these compounds on the studied catalysts is a zero order reaction. In Table 1 are given the values that characterize the ratios of the rate constants for the hydrogenation (k_0) of the C=C bond and the NO[•] group, which were obtained from the experiments on the hydrogenation of radical (I), compounds (VIII) and (IX), and their binary mixture. As can be seen, for the same catalyst the ratios of the reaction rates are practically independent of whether the reduced groups are found in one molecule or in different molecules. The same sequence in the reduction of the C=C bond and NO[•] group is retained when binary mixtures of (VIII) and (IX) are hydrogenated as when radical (I) is hydrogenated.

In Table 2 are given the ratios of the adsorption coefficients for (VIII) and (IX), which were calculated from the equation

$$\frac{\lg C_{0(\text{VIII})}/C_{i(\text{VIII})}}{\lg C_{0(\text{IX})}/C_{i(\text{IX})}} = \frac{k_{0(\text{VIII})}}{k_{0(\text{IX})}} \cdot \frac{b_{0(\text{VIII})}}{b_{i(\text{IX})}}$$





TABLE 2. Ratio of Adsorption Coefficients $b_{(IX)}/b_{(VIII)}$ of Radical (IX) and Methyl p-Vinylbenzoate (VIII) when Hydrogenated as a 1:1 Binary Mixture. Solvent = Alcohol, Temperature = 20°C.

Catalyst	^b (IX) ^{/b} (VIII)				
Skeletal Ni	74,0				
Pt-black	6,4				
Rh-black	3,7				
Pd-black	≪0,1				

where $C_{0(VIII)}$ and $C_{0(IX)}$ are the starting concentrations of (VIII) and (IX), and $C_{i(VIII)}$ and $C_{i(IX)}$ are their running concentrations.

From Table 2 it can be seen that the molecules that contain nitroxyl groups are preferentially adsorbed on the Ni and Pt catalysts, while the compounds with an olefinic bond are adsorbed preferentially on Pd.

It is obvious that the reaction sequence when (I) is hydrogenated on nickel is determined mainly by adsorption factors. In the first step radical (I) is adsorbed via its nitroxyl group, and the formed unsaturated substituted hydroxylamine is displaced from the catalyst surface by the molecules of the starting compound. In the second step (in the absence of the NO° group) the molecules

are adsorbed via the C=C bond, which is hydrogenated at a fast rate. The NOH group is reduced very slowly



The high selectivity for the hydrogenation of the NO[•] group of radical (I) on Pt is apparently also explained by the preferential adsorption of the radical centers.

The established sequence of the reactions on the studied catalysts is also retained when the paramagnetic esters of acrylic (II) and methacrylic acids (III) are hydrogenated (Fig. 3).

It is known that the reactivity of olefins during catalytic hydrogenation depends on the degree of substitution of the C=C bond. It seemed interesting to ascertain if di- and trisubstituted C=C bonds can also be selectively reduced in the presence of the nitroxyl group on Pd catalyst.

Since the above given results revealed that the sequence and selectivity of the reactions is independent of whether the NO' group and the C=C bond are found in one or different molecules, experiments were run with binary mixtures that contained radical (IX) and monoolefins (Table 3). From Table 3 it can be seen that in a mixture with radical (IX) the cis-isomer of the β -olefin is reduced just as selectively as the α -olefin. However, the selectivity decreases noticeably for the trans-isomer of the β -olefin, while an olefin with a trisubstituted C=C bond (2-methyl-2-butene) is reduced simultaneously with radical (IX).



Fig. 3. Change in catalyzate composition when radical (II) is hydrogenated on Pd-black: 1) paramagnetic ester of acrylic acid (II); 2) paramagnetic ester of propionic acid (X); 3) substituted hydroxylamine of propionic acid.

H, g-atom

TABLE 3. Selectivity of Hydrogenation S of Radical in Binary Mixture with Olefins on Pd-Black. Solvent=Alcohol, Temperature = 20°.

Olefin	$S = v_{C} = C/$ / v_{NO} .
1-Pentene cis-2-Pentene trans-2-Pentene 2-Methy1-2-butene	$\begin{array}{c} 0,99\\ 0,95\\ 0,70\\ 0,40 \end{array}$

It is known that on Pd and Ni, due to preferential adsorption, dienic hydrocarbons are reduced selectively in a mixture with olefins [3]. Experiments on the hydrogenation of isoprene in a mixture with radical (IX) revealed that on Ni the molecule with a nitroxyl group is adsorbed more firmly on the catalyst; the radical centers are selectively reduced in the presence of the diene, which is then hydrogenated at a fast rate (Fig. 4). In contrast to this, on Pd the diene is reduced first, and then the α -olefins or reaction products. Radical (IX) enters into reaction only in the step where 2-methyl-2-butene remains in the solution.

Previously it was shown [4] that nitroxyl biradicals are reduced

in sequence on metals of the platinum group, evidently due to the stronger adsorbability of the molecules with two radical centers. Experiments on the hydrogenation of the di-(2,2,6,6-tetramethyl-1-oxyl-4-piperidyloxy)-o-phthalate biradical in a mixture with isoprene make it possible to establish the reaction sequence of these compounds on Ni and Pd catalysts

Ni: biradical > monoradical > diene > olefins Pd: diene > α -olefins > disubstituted β -olefins > biradical > monoradical, trisubstituted olefins

As a result, Raney Ni can be used for the selective reduction of the nitroxyl groups of mono- and biradicals in the presence of C=C and C=C-C=C bonds, while Pd can be used for the reduction of the diene group and α -olefins (without involving the radical centers).

It is known that the triphenylphosphine complex of rhodium $(RhCl(PPh_3)_3)$ is highly active in the reduction of the double bond of α -olefins, but it does not accelerate the reduction of the nitro group [5]. It



Fig. 4. Hydrogenation of mixture of radical (IX) and isoprene on Ni catalyst: a) kinetic curve; b) change in catalyzate composition. 1) Radical (IX); 2) substituted hydroxylamine (XIV); 3) isoprene; 4) 3-methyl-1-butene; 5) 2-methyl-1-butene; 6) 2-methyl-2-butene; 7) isopentane.

proved that the vinyl group of ester (VIII) in a mixture with (IX) is reduced at a fast rate, after which the reaction stops. Radical (IX) when taken separately is also not hydrogenated in the presence of RhCl(PPh₃)₃.

EXPERIMENTAL METHOD

2,2,6,6-Tetramethyl-1-oxyl-4-piperidyloxy-p-vinylbenzoate was obtained from p-vinylbenzoyl chloride and 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl. Recrystallization from hexane gave orange crystals with mp 59°; mol. wt. 302 (by mass spectrometry).

Methyl p-vinylbenzoate was obtained by the esterification of the acid (prepared and described in [6]) with methanol, saturated with HCl (10%), mp 36° [7].

The paramagnetic esters of acrylic and methacrylic acids were synthesized as described in [8], mp respectively 102 and 88°. 2,2,6,6-Tetramethyl-4-hydroxypiperidine-1-oxyl was obtained as described in [9], mp 70°.

The Pt-, Pd-, and Rh-blacks were prepared by the reduction of $PdCl_2$, H_2PtCl_6 , and $RhCl_3 \cdot 3H_2O$ with formaldehyde in alkaline medium. The Raney Ni was obtained by leaching the 50:50 Ni-Al alloy with 20% NaOH solution. The RhCl(PPh₃)₃ was synthesized as described in [10].

The hydrogenation was run in a thermostated hydrogenation vessel at 20° , atmospheric H₂ pressure, and intense mixing (700 turns/min) in methanol medium. For each experiment we took $3 \cdot 10^{-3}$ mole of substance in 20 ml of solvent, and either 0.05 g of the black or 0.10 g of Raney Ni. In the case of RhCl-(PPh₃)₃ a 1:1 benzene-ethanol mixture was used as the solvent.

The chromatographic analysis was run on an LKhM-8MD instrument equipped with a flame-ionization detector.

It was difficult to analyze the hydrogenation products of radical (I) due to their low volatility and instability at the analysis temperature. An indirect method was developed, which included the prior transesterification of the catalyzate sample with methanol and subsequent analysis of the formed mixture of the methyl esters of p-vinyl- and p-ethylbenzoic acids. To analyze the esters we used a column packed with 15% poly(ethylene glycol succinate) deposited on Chromosorb W and a temperature of 130° . The method makes it possible to quantitatively determine the extent to which radical (I) is hydrogenated at the C=C bond.

To analyze the hydrogenation products of the paramagnetic esters of the acrylic and methacrylic acids we used 10% of Triton 305X deposited on Chromosorb W as the stationary phase and a temperature of 120°. The selected conditions make it possible to separate the unsaturated paramagnetic esters (II) and (III) from the corresponding esters of the saturated acids (X) and (XI). Analysis of the components that emerge from the chromatographic column by EPR revealed that the radical centers of the esters are re-tained. However, the substituted hydroxylamines (XII) and (XIII) give peaks that coincide with the peaks of the corresponding radicals, probably due to oxidation during the analysis process.

The EPR analysis was run on an EPR-2 spectrometer designed by the Institute of Chemical Physics. To prevent oxidation of the formed substituted hydroxylamines the catalyzate samples were removed and sealed in ampules in an argon atmosphere. It also proved convenient to remove the samples into AcOH, which combines with the easily oxidized substituted hydroxylamines.

The data that characterize the previously unknown radical (I), and the partially reduced products (IV), (V), (VI), and (VII) that were isolated from it, are given in Table 4. 2,2,6,6-Tetramethyl-1-oxyl-4-piperidyloxy-p-ethylbenzoate was isolated when radical (I) was hydrogenated on Pd after the absorption of

		Found, %			Calculated, %		IR spectrum (ν , cm ⁻¹)			st		
Com - pound	T, mp °C	с	н	N	Empirical formula	С	н	N	C=C	он	NH	Cataly
(I) (IV) (V) (VI) (VII)	59,0 109,5 81,5 87,0 80,0	70,63 70,95 71,0 70,8 74,74	$8,20 \\ 8,70 \\ 8,60 \\ 8,85 \\ 9,34$	$4,60 \\ 4,67 \\ 4,60 \\ 4,59 \\ 4,84$	C ₁₈ H ₂₄ NO ₃ C ₁₈ H ₂₅ NO ₃ C ₁₈ H ₂₆ NO ₃ C ₁₈ H ₂₇ NO ₃ C ₁₈ H ₂₇ NO ₂	71,50 71,28 70,95 71,3 74,74	8,00 8,25 8,71 9,2 9,34	$4,63 \\ 4,62 \\ 4,68 \\ 4,74 \\ 4,83$	1635 1635 	3480 	 3320	— Pt Pd Pt Ni

TABLE 4. Characteristics of Obtained Compounds

1 mole of H₂. Recrystallization from hexane gave the compound as orange crystals in $\sim 100\%$ yield. The EPR spectrum shows that the radical center is retained. Only the peak of (V) is observed on the chromatogram after transesterification with methanol.

The unsaturated hydroxylamine of 2,2,6,6-tetramethyl-1-oxyl-4-piperidyl-p-vinylbenzoic acid was obtained by the hydrogenation of radical (I) on either Ni or Pt. White crystals were isolated from the catalyzate after the absorption of 0.5 mole of H_2 . Only traces of radical (I) were detected in the solution by EPR.

2,2,6,6-Tetramethyl-1-hydroxy-4-piperidyloxy-p-ethylbenzoate (VI) was obtained by the hydrogenation of radical (I) on Pt, and also on Pd or Rh. The reaction stops spontaneously after the absorption of 1.5 moles of H₂. White crystals were isolated in ~100% yield from the solution after removing the catalyst and evaporation.

2,2,6,6-Tetramethyl-4-piperidyloxy-p-ethylbenzoate was obtained by the hydrogenation of radical (I) on Ni, and white crystals were isolated from the solution after the absorption of 2.5 moles of H₂.

The properties of the products, obtained by the hydrogenation of (I), are given in Table 4.

The paramagnetic esters of the propionic and isobutyric acids (X) and (XI) were obtained by the respective hydrogenation of (II) and (III) on Pd. Analysis of the catalyzate during reaction by GLC reveals that the peak of the starting radical (II) or (III) decreases in harmony with the amount of absorbed H_2 and a new peak appears, which corresponds to radical (X) or (XI). The EPR spectrum of the product corresponds to the spectrum of radical (II) or (III). The bands for the C=C bond and the OH group (which characterize the starting radical and the substituted hydroxylamine) are absent in the IR spectrum.

The substituted unsaturated hydroxylamines (XII) and (XIII) were obtained by the hydrogenation of (II) and (III) on either Ni or Pt catalyst. The reaction products do not give EPR signals, while the IR spectra have bands at 1640 and 3480 cm⁻¹, which characterize the C=C bond and OH group.

CONCLUSIONS

1. The hydrogenation of unsaturated stable radicals, the paramagnetic esters of the p-vinylbenzoic, acrylic, and methacrylic acids, on Pd-black or in the presence of $RhCl(PPh_3)_3$, proceeds stepwise. The C=C bond is reduced in the first step of the reaction without involving the paramagnetic center.

2. On Raney Ni and Pt catalysts the radical center and C=C bond are reduced in sequence due to the preferential absorption of the nitroxyl group of the molecule.

3. The established sequence of the reactions on Pd catalyst is also retained when mixtures of olefins and the nitroxyl radical (IX) are hydrogenated, and here the selectivity of the process depends on the degree of substitution of the C=C bond.

4. Some previously unknown unsaturated substituted hydroxylamines and stable nitroxyl radicals were obtained by catalytic hydrogenation.

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