

## SELECTIVE HYDROGENATION OF AROMATIC AND ALIPHATIC NITRO COMPOUNDS BY HYDROGEN TRANSFER OVER MgO

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## SUMMARY

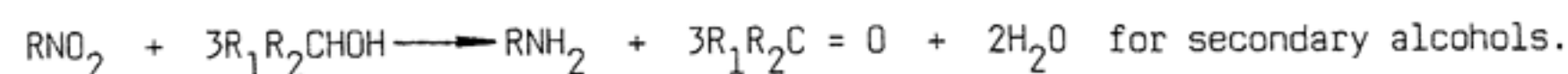
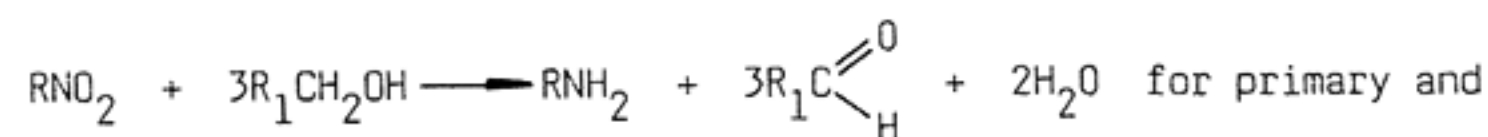
The possibility of using of aliphatic alcohols as hydrogen donors for the catalytic transfer reduction of nitro group over MgO was examined. Catalytic hydrogen transfer was found to be effective and selective method for reduction of nitrobenzene, 4-nitrotoluene, 4-chloronitrobenzene, 4-nitro-m-xylene,  $\beta$ -nitrostyrene, 3-nitrobenzaldehyde, 1-nitropropane, and 1-nitrobutane. Conversion of starting nitro compound into desired product depended on the alcohol used as a donor. Adsorption of reactant and catalyst deactivation were studied by esr. New aspects of a role of one-electron donor sites in hydrogen transfer over MgO were demonstrated.

## INTRODUCTION

Commercially nitroarenes and nitroalkanes are reduced to corresponding amines on non-catalytic (using Bechamp or Zinin method) or on catalytic way (hydrogen gas over metals). The catalytic transfer hydrogenation is an effective alternative for the above methods. Reductions of nitroarenes to aminoarenes by hydrogen transfer was reported for a wide range of metallic catalysts such as Pd, Cu, Fe, Ni, Rh and Ru (ref. 1). In a search for active hydrogen donors, it was found that formic, phosphinic and phosphorous acids, and their salts, unsaturated hydrocarbons as cyclohexene, and especially hydrazine would reduce nitro compounds to amines with satisfying yield (ref. 1). The only but important limitation of the process is the high price of donors used.

In the present paper we have examined the possibility of using of alcohols as hydrogen donors for catalytic transfer reduction (CTR) of nitro group. This paper is the continuation of our previous efforts at studying the synthetic application of hydrogen exchange on oxides. Our recent results concerned the reduction of aldehydes (saturated and unsaturated), epoxides, and nitriles, as well as the dehydrogenation of long chain aliphatic alcohols and alkylaromatics (ref. 2). The reduction of a series of aromatic and aliphatic nitro compounds with various alcohols was studied over magnesium oxide as the catalysts.

The hydrogen transfer reaction between alcohols and nitrocompounds should proceed according to the following equations:



In both cases the minimum donor - acceptor molar ratio demanded for the reduction of nitro- to amino group equals 3.

## EXPERIMENTAL

Reactions were carried out in a continuous fixed bed reactor at atmospheric pressure in the temperature range 350-450°C with MgO as a catalyst. The radical properties of the fresh, deactivated and regenerated catalyst, as well as the adsorbed states of reactants were studied by esr using Radiopan SE/X 2547 spectrometer. The adsorption of reactants was performed according to the procedure described elsewhere (ref. 3). The magnesia catalyst preparation was described previously (ref. 3). The liquid product mixtures were analysed by gc (Chrom 5) using 4-m glass column filled with 20 % OV-101 on Gas Chrom Q. Products were characterized by comparison with authentic samples (ir, gc) and by melting points of their hydrochlorides.

## RESULTS AND DISCUSSION

The  $K_p$  values for the reactions of hydrogen transfer between primary and secondary alcohols and nitro compounds were calculated using Van Krevelen and Chermin procedure (ref. 4). Similarly as the simple reduction with hydrogen the catalytic hydrogen transfer from alcohols to nitro derivatives is strongly favored thermodynamically. For all studied reactions with primary alcohols the  $K_p$  values were of the range of  $10^{35}$ , while for processes involving secondary alcohols  $K_p \sim 10^{44}$ .

### Reduction of nitroarenes

Magnesium oxide exhibited high activity and high selectivity in the hydrogen transfer from alcohols to studied nitroarenes. Because of the limited space of the paper the complete amine yield - temperature dependence was shown only for nitrobenzene reduction (Table 1). However, also for other reactants the yield of the aminic product increased continuously between the values obtained at the lowest (350°C) and the highest (450°C) reaction temperatures. Below 350°C the complete lack of activity of MgO in the studied transformation was noted. The same was observed by us earlier (ref. 2) in the case the catalytic transfer reduction of other functional groups.

(i) Reduction of nitrobenzene. The conversion of nitrobenzene into aniline depended strongly on the alcohol used as a hydrogen donor. Unexpectedly, methanol was the most effective donor molecule (91.4 % of aniline). The order of ac-

tivity for hydrogen donation was found to be methanol  $\sim$  isopropanol  $>$  s-butanol  $>$  n-propanol  $>$  ethanol  $>$  n-butanol  $>$  i-butanol.

(ii) Reduction of other nitroarenes. Table 2 depicts the yields of amines formed by reduction of the studied nitroarenes. No general rule of usefulness of particular alcohols for the reduction process was observed. Maximum yield of p-toluidine (39.8 %) was gained in the reaction of 4-nitrotoluene with n-butanol. Highest conversion of 4-nitro-m-xylene into 4-amino-m-xylene was obtained using isopropanol as a donor molecule, while the most effective action of ethanol was noted in the reduction of 4-chloronitrobenzene (62.8 % of 4-chloroaniline). It should be underlined that all studied reactions occurred with the selectivity higher than 99 %, only traces of condensation tar-like products were detected in the products mixture. The ease of reduction decreased in the order 4-chloronitrobenzene  $>$  4-nitrotoluene  $>$  2,4-dimethylnitrobenzene. The above observation led us to the preliminary conclusion that the electronegative character of the substituent diminishes fitness of nitro group in nitroarene on the reduction.

(iii) Reduction of nitroarenes possessing second reducible group. The products distributions of the reduction of  $\beta$ -nitrostyrene and 3-nitrobenzaldehyde with various alcohols are listed in Table 3.  $\beta$ -Phenylethylamine (I) - the product of total reduction of side chain as well as both products of its partial reduction:  $\beta$ -phenylvinylamine (II) and  $\beta$ -phenylnitroethane (III) were obtained in the reaction of  $\beta$ -nitrostyrene. The type of a donor used strongly affected the reaction selectivity. E.g. using methanol as hydrogen donor the ratio of I : II : III (450°C) was 41.2 : 49.0 : 8.4 (at the conversion of reactant - 100 %), the same ratio was 12.1 : 67.1 : 18.8 (at the reactant conversion of 98.0 %) for isopropanol (350°C), and 30.1 : 42.3 : 15.4 (at the conversion of  $\beta$ -nitrostyrene of 97.8 %) for s-butanol. The greater ease of reduction of nitro group in comparison with C=C bond reduction is obvious, however, the presence of remarkable amounts of  $\beta$ -phenylethylamine in reaction products indicates that exchange of -NO<sub>2</sub> group accelerates the reduction of a neighbour vinyl group. It should be emphasized that the reduction of  $\beta$ -nitrostyrene by catalytic transfer reduction leads to the products completely different than these obtained in hydrogen transfer over metals. Namely, reduction of  $\beta$ -nitrostyrene with formic acid over palladium gave the oxime of phenylacetaldehyde (ref. 5).

Much more spectacular were the selectivity variations in the case of 3-nitrobenzaldehyde reduction (Table 3). Depending on the hydrogen donor used 3-nitrobenzyl alcohol (methanol, 450°C) or 3-aminobenzaldehyde (i-propanol, 450°C) were the main reaction products.

### Reduction of nitroalkanes

The effectiveness of catalytic transfer hydrogenation of nitroparaffins over MgO is demonstrated in the Table 4. At 450°C 1-nitropropane yielded 94.9 % of

TABLE 1  
The yields of aniline formed in the reaction of nitrobenzene with various alcohols over MgO, HLSV-1

Reaction temperature °C	Donor/acceptor ratio	Yield of aniline using a given donor mol %					
		methanol	ethanol	n-propanol	i-propanol	n-butanol	i-butanol
350	3 : 1	77.3	26.1	15.8	62.5	12.3	30.0
375	3 : 1	77.8	30.9	26.5	73.9	18.2	33.1
400	3 : 1	78.4	38.3	33.6	74.5	22.6	41.2
425	3 : 1	81.5	39.1	39.3	78.3	25.6	50.0
450	3 : 1	91.4	47.3	51.3	91.0	37.1	54.4

TABLE 2

The yields of amines formed in the reactions of corresponding nitroarenes with various alcohols over MgO, donor : acceptor ratio-3, HLSV-1

Reactant	Reaction temperature °C	Yield of amine using a given donor mol %					
		methanol	ethanol	n-propanol	i-propanol	n-butanol	i-butanol
4-nitrotoluene	350	18.1	14.4	11.7	12.5	13.9	13.8
	450	24.2	33.7	28.3	29.6	39.8	27.4
2,4-dimethylnitrobenzene	350	7.3	16.6	6.3	tr	tr	tr
	450	13.7	31.0	18.2	16.0	20.7	20.7
4-chloronitrobenzene	350	19.0	38.0		25.1		18.4
	450	32.4	58.1		63.6		45.7

TABLE 3

The products of the reduction of nitroarenes possessing a second reducible group with various alcohols over MgO, donor : acceptor ratio-6, HLSV-1

Hydrogen donor	Reaction temperature °C	Products of $\beta$ -nitrostyrene reduction mol %		Products of 3-nitrobenzaldehyde reduction mol %			
		$\beta$ -phenyl-ethylamine	$\beta$ -phenyl-1-vinylamine	$\beta$ -phenyl-1-troethane	3-aminobenzyl alcohol	3-aminobenzaldehyde	3-nitrobenzyl alcohol
methanol	350	41.3	35.8	14.3	2.8	-	-
	450	41.2	49.0	8.4	13.6	-	82.6
ethanol	350	18.7	44.0	21.2	2.0	5.7	-
	450	20.4	49.9	29.0	35.1	8.9	36.0
n-propanol	350	19.4	45.1	30.5			
	450	36.4	28.2	20.3			
i-propanol	350	12.1	67.1	18.8	2.7	1.5	-
	450	22.1	47.1	25.2	14.8	57.6	7.0
s-butanol	350	15.4	42.3	30.1			
	450	20.2	46.4	32.3			

TABLE 4

The yields of corresponding amines formed in reactions of 1-nitropropane and 1-nitrobutane with various alcohols, donor : acceptor ratio-3, HLSV-1

Reactant	Reaction temperature °C	Yield of amine using a given donor mol %					
		methanol	ethanol	n-propanol	i-propanol	n-butanol	i-butanol
1-nitropropane	350	4.3	18.6	10.6	9.3	35.5	3.7
	450	67.5	76.5	41.2	94.9	84.9	76.3
1-nitrobutane	350	11.1	23.8	9.6	9.8	8.7	6.3
	450	83.7	87.9	90.9	79.0	76.9	53.8



1-propylamine with  $\sim 100\%$  selectivity (isopropanol). At the same temperature 1-nitrobutane was converted to 1-butylamine with yield of 93.5% and 100% selectivity (isobutanol).

#### Catalyst deactivation and regeneration

The catalyst decay during nitrobenzene reduction was studied in long-time experiments. The gradual poisoning of the catalyst was observed (Table 5) which led in 4-5 hrs to the significant diminishing of reactant conversion.

TABLE 5  
The decrease of aniline yields (mole %) during nitrobenzene reduction with various alcohols, temperature - 450°C, donor : acceptor ratio-3, HLSV-1

Time on stream hr	0	1.0	2.0	3.0	4.0	5.0	20.0
Hydrogen donor							
methanol	91.4	69.1	57.7	36.0	18.6	10.6	10.0
isopropanol	91.0	46.5	25.3	13.8	12.0	9.6	10.4
isopropanol(N <sub>2</sub> ) <sup>1</sup>	91.0	91.3	90.8	54.0	32.1	21.0	
isopropanol(O <sub>2</sub> ) <sup>2</sup>	91.0	90.7	91.4	90.3	91.0	90.9	90.7
n-propanol	51.3	37.4	16.5	15.3	9.5		9.1
s-butanol	54.4	32.6	17.4	11.2	8.8		8.3

1-catalyst regenerated by nitrogen (450°C) treatment during 10 min after each 30 min of reaction, 2-catalyst regenerated by air treatment according the same procedure

Depending on the used alcohol the deactivation profiles reached the plateau corresponding the yield of aniline in the range of 8-10 mol %. Various regeneration procedures have been applied to preserve the catalyst activity on the high level. The calcination of used catalyst during 10 min in air at 450°C following each 0.5 hr of catalyst work was found to be the optimum regeneration mode (Table 5). The heating in neutral gas (nitrogen or argon) did not result in satisfying activity stability. The same regeneration procedure as for nitrobenzene was successfully adopted in reduction of other investigated nitroarenes.

#### Esr studies of surface intermediates

In our previous paper (ref. 2) we demonstrated the particular role played by one-electron donor centres on magnesia surface in catalytic transfer hydrogenation. Moreover, nitroarenes exhibit high tendency to convert themselves into corresponding anion radicals during adsorption on MgO. Thus, it was expected that esr spectroscopy would reveal new data concerning the reactants activation.

Esr investigations were done of catalysts samples with reactants adsorbed at room and at reaction temperature. Also the preparations of deactivated and regenerated catalyst were studied. From all studied nitro compounds only the following: nitrobenzene (parameters of esr signal:  $g = 2.0031$ ;  $\Delta H_{\max} = 7$  Gs; intensity  $1.2 \cdot 10^{17}$  spin  $\cdot$  g<sup>-1</sup>), m-dinitrobenzene ( $2.0043$ ; 9 Gs;  $1.9 \cdot 10^{18}$  spin  $\cdot$  g<sup>-1</sup>), 4-nitrotoluene ( $2.0051$ ; 10 Gs;  $6.1 \cdot 10^{18}$  spin  $\cdot$  g<sup>-1</sup>), 4-nitro-m-xylene ( $2.0031$ ; 13 Gs;  $1.8 \cdot 10^{19}$  spin  $\cdot$  g<sup>-1</sup>), formed the corresponding anion radicals. None from the used alcohols was converted into paramagnetic species on MgO surface.

New evidence for the importance of one electron donor centres for catalytic transfer reduction has arisen from esr investigations. Both, heating of anion

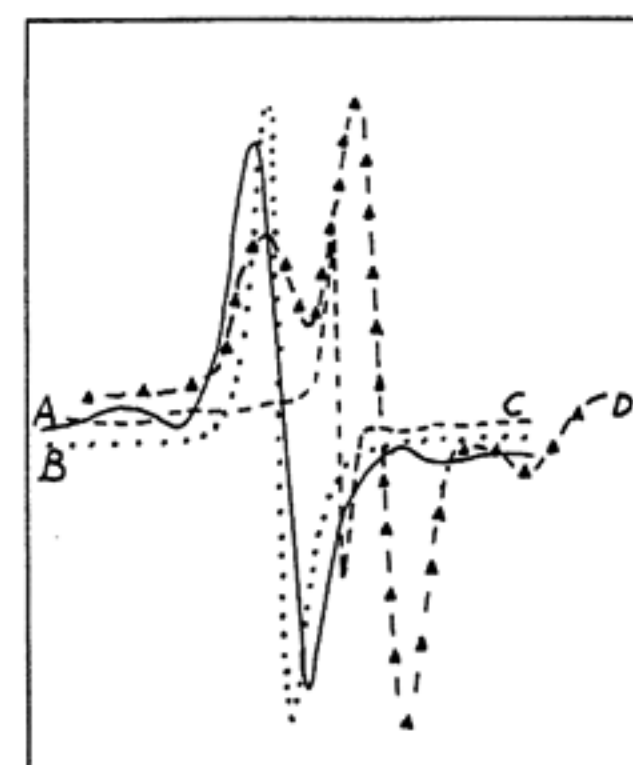


Fig. 1. Esr of paramagnetic species on deactivated and regenerated catalyst surface.

radical of nitrobenzene on MgO surface from room temperature to 350°C, or adsorption of nitrobenzene at 350°C on fresh MgO resulted in the new paramagnetic species. Esr signal (A on Fig. 1) of this species differed in shape (lack of h.f.c. structure) and in  $g$  value ( $g = 2.0023$ ) from the signal of the parent ion radical, intensity remained only slightly changed. During the reaction of nitrobenzene with alcohol surface species underwent further evolution and esr spectrum of MgO after 5 hrs of reaction revealed the presence of a narrow signal ( $\Delta H_{\max} = 4$  Gs,  $g = 2.0023$ ) of the intensity c.a. 600 times higher than the one measured for the ion radical (B on Fig. 1). Most probably the new signal derived from radicals formed in a surface chain reaction of adsorbed reactants. During regeneration by air treatment the number of surface radical species remarkably diminished, the esr spectrum (C on Fig. 1) of regenerated catalyst consisted from the narrow signal ( $\Delta H_{\max} = 3$  Gs,  $g = 2.0030$ ) which intensity corresponded to only  $8 \cdot 10^{17}$  spin  $\cdot$  g<sup>-1</sup>. The one-electron donor properties of deactivated and regenerated catalyst were controlled using nitrobenzene (electron affinity 0.7 eV) and m-dinitrobenzene (E.A. 1.4 eV) adsorption. The adsorption of nitrobenzene on both deactivated and regenerated surfaces did not lead to the appearance of a new paramagnetic surface species. The same result was noted when n-dinitrobenzene adsorbed on deactivated magnesia. However, m-dinitrobenzene adsorption on regenerated MgO surface resulted in the formation of a typical radical species ( $g = 2.0043$ ,  $\Delta H_{\max} = 12$  Gs, intensity  $1.2 \cdot 10^{18}$  spin  $\cdot$  g<sup>-1</sup>) (D on Fig. 1). This observation led us to the conclusion that from strong and moderate donor sites present on MgO surface (Ref. 3), only the second one would be easily regenerated and exhibit activity in studied reactions.

Strong centres, forming anion radical even from nitrobenzene molecule are poisoned irreversibly, however, their presence is not necessary for the preservation of catalytic activity. Taking into consideration that regenerated MgO which is not able to ionize nitrobenzene molecule is still active in its reduction by hydrogen transfer and that only a few from reduced nitro compounds form ion radicals on catalyst surface one can ascertain that ion radicals formation is not necessary step in nitroarenes (or nitroparaffins) activation. Probably, one-electron donor sites take part only in activation of alcohol what was demonstrated by us earlier.

#### CONCLUSION

The main conclusions would be summarized as following:

- (i) the reduction of nitro compounds with alcohols by catalytic hydrogen transfer is a very selective process;
- (ii) the conversion of starting nitro compounds into desired products depends on the alcohol used as a donor. Each reaction should be individually optimized to find the most effective donor molecule. The substitution in nitroarene molecule diminishes its reactivity in catalytic transfer reduction (CTR);
- (iii) the previously demonstrated (ref. 2) action of one-electron donor sites on MgO surface is limited to the donating alcohol transformation; ionization of nitro compound molecule is not necessary step of its activation for CTR;
- (iiii) the simplicity of reaction, accessibility of reactants and ease of catalyst regeneration make CTR of nitro group with alcohols over MgO useful method for the commercial selective synthesis of aryl and alkylamines.

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