

REDUCTION OF METAL CARBONYLS WITH A MODEL FOR NADH

AMITABHA BASU, SUMIT BHADURI* and KRISHNA R. SHARMA

Alchemie Research Centre, CAFI Site, P.O. Box 155, Thane-Belapur Road, Thane 400 601, Maharashtra (India)

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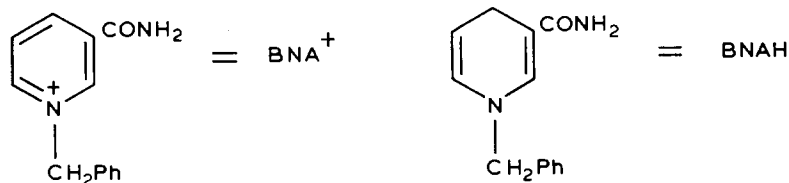
Summary

N-benzyl 1,4-dihydronicotinamide (BNAH) acts as an efficient hydride donor in its reactions with mono and polynuclear metal carbonyls. Formation of stable hydrido carbonyls is considered to be responsible for the absence of catalytic activity of $\text{Ru}_3(\text{CO})_{12}$ (I) and $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ (II) in transfer hydrogenation reactions involving BNAH as the donor.

Introduction

Nicotinamide nucleotide, NADH, plays an important role in a number of biological redox reactions. This coenzyme serves as the transient intermediate carrier of a hydride ion that is enzymatically removed from a substrate molecule by the action of certain hydrogenases. Enzymic and non-enzymic catalytic systems involving NADH or models of NADH and transition metal complexes have been reported [1,2].

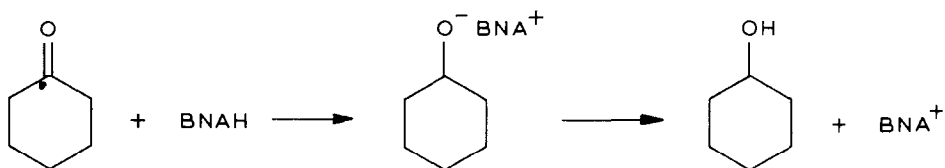
Horse liver alcohol dehydrogenase has been shown to be effective in catalysing the conversion of cyclohexanone into cyclohexanol with NADH as the donor molecule [2]. *N*-benzyl 1,4-dihydronicotinamide (BNAH) and the oxidised nicotinamide moiety (BNA^+) have been widely used as models for NADH and NAD^+ respectively.



Carbonyl clusters such as $\text{Ru}_3(\text{CO})_{12}$ and $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ are known to catalyse a variety of transfer hydrogenation reactions in which the donor molecules are usually primary or secondary alcohols [3]. We wanted to see if BNAH, a known model for NADH, could be used as the donor molecule in transfer hydrogenation reactions catalysed by ruthenium carbonyl clusters. Failure to find examples of such participation by BNAH prompted us to explore the nature of interaction between BNAH and some mono and polynuclear metal carbonyls. These results are described here.

Results and discussion

Neither I nor II catalyses the reduction of cyclohexanone with BNAH as the donor, such reactions should lead to the formation of cyclohexanol, as shown below:



Carrying out the reaction in the presence of an appropriate amount of water or work-up involving treatment with dilute hydrochloric acid did not give any detectable quantities of cyclohexanol.

The conclusion is that the first step, the hydride transfer from BNAH to cyclohexanone is not catalysed by the ruthenium clusters. In the absence of protic solvents, IR monitoring of the reaction mixture indicates the formation of $[\text{HRu}_3(\text{CO})_{11}]^-$ (III) and $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ (IV) from I and II, respectively. A stoichiometric reaction between II and BNAH yielded analytically pure $[\text{BNA}][\text{H}_3\text{Ru}_4(\text{CO})_{12}]$. A similar reaction involving BNAH and $\text{Ru}_3(\text{CO})_{12}$ appears to give $[\text{BNA}][\text{HRu}_3(\text{CO})_{11}]$, as indicated by the IR spectrum of the solution obtained.

Both I and II can be used as effective precatalysts for the conversion of cyclohexanone into cyclohexanol in isopropanol containing BNAH. However, in these cases the donor is isopropanol and not BNAH, as is evident from the formation of acetone and quantitative recovery of BNAH at the end of the reaction.

It is important to note that the observed catalytic activities are higher than those of systems not involving BNAH and based only on I or II. This is due to the fact that the anionic species III and IV are catalytically more active than I or II. The catalytic behaviour of III and IV in a variety of conventional transfer hydrogen reactions with alcohols as donors will be described elsewhere.

The results described above show that BNAH donates hydride ions to ruthenium carbonyls. It also provides the oxidised nicotinamide moiety BNA^+ as the counterion for the resultant anionic carbonyl clusters. To extend the scope of this reaction and to test its generality BNAH was treated with some other carbonyl clusters.

Carbonyl cluster anions of platinum $[\text{Pt}_3(\text{CO})_6]_n^{2-}$ ($n = 6, 5, 4$) are known to undergo stepwise reduction by hydrogen or water to give $[\text{Pt}_9(\text{CO})_{18}]^{2-}$, protons, and, in the case of water, oxygen [4,5]. No hydride intermediates have so far been

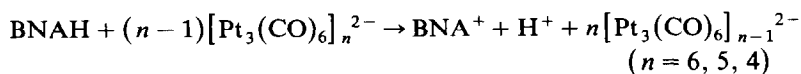
TABLE 1

RESULTS OF THE REACTIONS OF BNAH WITH MONO AND POLYNUCLEAR METAL CARBONYLS

Starting material	Product	Yield ^a (%)
M ₃ (CO) ₁₂ (M = Fe, Ru)	[BNA][HM ₃ (CO) ₁₁]	80
H ₄ Ru ₄ (CO) ₁₂	[BNA][H ₃ Ru ₄ (CO) ₁₂]	90
[Pt ₃ (CO) ₆] _n ²⁻ (n = 6, 5, 4)	[Pt ₉ (CO) ₁₈] ²⁻	90
M(CO) ₆ (M = Cr, Mo)	[BNA][HM ₂ (CO) ₉]	60

^a Yields are based on isolated material for [BNA][H₃Ru₄(CO)₁₂], and on IR spectral band intensities for the other products.

detected in these reactions. With BNAH as the reducing agent a similar pathway is followed:



The platinum cluster anions have highly characteristic UV-VIS spectra and the above reactions can be conveniently monitored by spectrophotometry [5].

The results of the reactions of BNAH with mono and polynuclear metal carbonyls are shown in Table 1. While BNAH has been found to be ineffective for the reduction of M₂(CO)₁₀ (M = Mn, Re) species, hydrido carbonyl anions of chromium and molybdenum were obtained from the corresponding hexacarbonyls.

Experimental

Infrared, NMR, and UV-VIS spectra were recorded on a Perkin-Elmer 377 grating spectrometer, a Bruker 80 MHz instrument, and a Pye-Unicam SP8 100 spectrophotometer, respectively. A Carlo Erba 1106 instrument was used for C, H and N microanalyses. Conversion of cyclohexanone into cyclohexanol was monitored by use of a Pye-Unicam 204 gas-liquid chromatograph. Ru₃(CO)₁₂, H₄Ru₄(CO)₁₂, [Pt₃(CO)₆]_n²⁻ and BNAH were synthesised by published procedures [6,7,4,1]. M(CO)₆ (M = Cr, Mo), M₂(CO)₁₀ (M = Mn, Re) and Fe₃(CO)₁₂ were purchased from Strem Chemicals, U.S.A. All reactions were carried out in dry freshly distilled solvents under an inert atmosphere.

Catalytic reactions

Reaction in acetonitrile. A mixture of BNAH (0.21 g, 1 mmol), cyclohexanone (0.1 g, 1 mmol), Ru₃(CO)₁₂ (0.013 g, 0.02 mmol) and acetonitrile (10 ml) was kept at 70°C for 3 h. GLC analyses at hourly intervals did not reveal any formation of cyclohexanol. IR monitoring of the reaction mixture suggested that [HRu₃(CO)₁₁]⁻ was the major (~ 80%) cluster carbonyl species in solution.

The same reaction when carried out in the presence of H₂O (0.02 g, 1 mmol) did not give any cyclohexanol. Work-up of a reaction mixture involving treatment with dilute HCl (5 ml) likewise gave no cyclohexanol.

Reaction in isopropanol. The reaction was carried out as above except that isopropanol was used in place of acetonitrile. Cyclohexanol and acetone (ca. 0.5 mmol by GLC) were detected at the end of the reaction. Removal of solvent and washing of the precipitate with cyclohexane gave BNAH (0.2 g) which was identified by comparing its IR, UV and NMR spectra with those of an authentic sample.

Reactions with $H_4Ru_4(CO)_{12}$ instead of $Ru_3(CO)_{12}$ as the catalyst were carried out under identical conditions. In acetonitrile formation of $[H_3Ru_4(CO)_{12}]^-$ was inferred from the IR spectra, whereas in isopropanol cyclohexanol and acetone (ca. 0.45 mmol) were detected.

Reaction of BNAH with metal carbonyls

Reaction with $H_4Ru_4(CO)_{12}$. A solution of BNAH (0.03 g, 0.15 mmol) and $H_4Ru_4(CO)_{12}$ (0.07 g, 0.1 mmol) in acetonitrile (10 ml) was kept at 70°C for 2 h then evaporated to dryness. The residue was extracted with dichloromethane, and addition of n-hexane to the extract gave $[BNA][H_3Ru_4(CO)_{12}]$ (Found: C, 31.0; H, 2.0; N, 2.8. $C_{25}H_{17}N_2O_{13}Ru_4$, calc: C, 31.3; H, 1.8; N, 2.9%), the identity of which was established by comparison of its spectrum with those for authentic $BNA^+ Cl^-$ and $[PPN][H_3Ru_4(CO)_{12}]$.

Reactions of $Ru_3(CO)_{12}$, $Fe_3(CO)_{12}$, $M(CO)_6$ ($M = Cr, Mo$), $M_2(CO)_{10}$ ($M = Mn, Re$) and $[Pt_3(CO)_6]_n^{2-}$ ($n = 6, 5, 4$) with BNAH were carried out similarly except that in the case of platinum clusters heating was avoided.

In all the cases the products were identified by solution spectral comparisons with authentic samples.

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