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INTRAMOLECULAR HYDROGEN TRANSFER IN ARENE COMPLEXES OF V, Cr AND Ni

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INTRODUCTION

Transition metal salts, such as vanadium(III) and chromium(III) chlorides, etc., can be reduced with alkali naphthalides in tetrahydrofuran (THF) solution. Variable amounts of low and zerovalent metal remain in the liquid phase whereas most of the reduced metal deposits as sponge[1,2].

A remarkable stabilization of the reduced metal in the liquid phase can, however, be obtained by merely reversing the reducing procedure, *i.e.*, adding the metal salt solution slowly to a moderate excess of the alkali naphthalide solution[2]. The stability of such a solution decreases somewhat with increasing population of the *d*-orbitals of the transition metal ion. Thus, vanadium was obtained with only 1–2% excess of naphthalide in a completely stable form and then used for kinetic work[3]. Nickel, on the other hand, shows a relatively poor stability under these conditions; after some minutes, Ni(0) sponge precipitates and the remaining black solution appears to be slightly ferromagnetic ($\chi_{At} = 20{,}000\text{–}80{,}000 \cdot 10^{-6}$ emu), indicating the presence of colloidal Ni(0) particles. The other first row transition metals show an intermediate stability behavior.

In the nickel case, however, a satisfactory stabilization is obtained if lithium naphthalide (LiNp) is employed in somewhat higher excess (LiNp/Ni >3, using $NiBr_2$ as starting material). Such solutions do not deposit any metal during several days, and no ferromagnetism is observed.

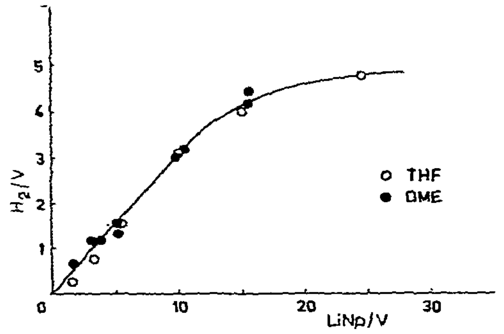
These observations indicate the metals to be present in an unusual state, presumably stabilized by complex formation. The present work was undertaken in order to obtain information concerning this unusual state. Hydrolysis, deuterolysis and mass spectroscopic analysis of the deuterolysis products, as well as electron paramagnetic resonance, have been used as experimental tools. Experiments with vanadium, chromium and nickel are reported in this paper.

RESULTS

(*a*) *Hydrolysis and deuterolysis*

Solutions of reduced vanadium, chromium or nickel (M), prepared by the reverse procedure[2] with LiNp in THF, evolve gas on hydrolysis, the amount of gas being a function of the ratio LiNp/M. Mass spectroscopy demonstrated this gas to be hydrogen. Fig. 1 shows the hydrogen evolution from reduced vanadium solutions.

Some experiments with another solvent, dimethoxyethane (DME), are included. In Fig. 2 the corresponding experiments with Cr and Ni are represented. In all cases the hydrogen evolution clearly increases with increasing ratio LiNp/M, although levelling off at LiNp/M > 10.



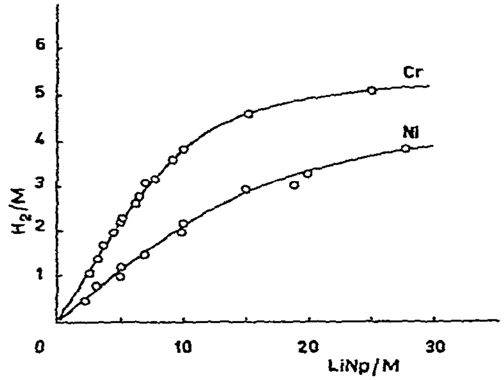


Fig. 1. Hydrogen evolution on hydrolysis of vanadium reduced with LiNp.

Fig. 2. Hydrogen evolution on hydrolysis of chromium and nickel, reduced with LiNp.

The use of heavy water for the hydrolysis allows some insight in the origin of the evolved gas. Results of the mass spectroscopic analysis of the deuterolytic gases are given in Table 1 (columns 3–5) for the three metals. From these data, in combination with the quantitative hydrolysis data (column 6), the amount of ^1H and ^2H evolved per metal atom can easily be computed. These data are shown in columns 7 and 8.

TABLE 1

ISOTOPE DISTRIBUTION OF THE GASEOUS PRODUCTS OBTAINED FROM THE DEUTEROLYSIS OF SOLUTIONS OF REDUCED METALS

Metal salt	*LiNp/M*	$^1H_2$ (%)	$^1H^2H$ (%)	$^2H_2$ (%)	H_2(total)/M[a]	$^1H/M$	$^2H/M$
VCl_3	3.1	31.4	18.8	49.8	1.0	0.80	1.20
	25.0	3.1	30.0	66.9	4.75	1.70	7.76 (6.95)[b]
$CrCl_3$	3.3	25.0	22.0	53.0	1.50	1.08	1.92
	6.3	4.0	36.0	60.0	2.75	1.21	4.29
	10.0	4.2	24.8	71.0	3.80	1.26	6.34
	25.0	6.8	25.2	68.0	5.05	1.95	8.15 (7.40)[b]
$NiBr_2$	2.1	100	0	0	0.50	1.00	0.0
	5.0	23.4	35.1	41.5	1.15	0.94	1.36
	30.0	4.0	20.0	76.0	3.90	1.08	6.72 (5.70)[b]

[a] See Figs. 1 and 2.

[b] Numbers in brackets are corrected for the ^2H evolution from the reaction of LiNp with heavy water; see *Experimental*.

In all cases the amount of ^2H evolved per metal atom increases with increasing ratio LiNp/M. The most complete set of data, that of Cr, indicates a levelling off with a probable limiting value of eight ^2H pro chromium atom (Fig. 3). The parallelism of the hydrolysis curves of V and Cr (Figs. 1 and 2), as well as the similarity of the few deuterolytic data of V with those of Cr allows the supposition that about eight ^2H per metal atom are also the highest attainable value for vanadium. In the nickel case this limiting value seems to be somewhat lower, probably about six ^2H per nickel atom.

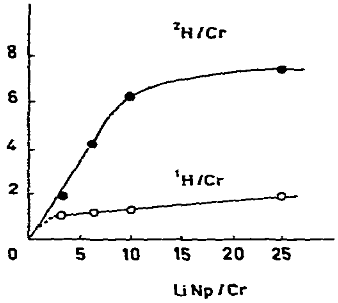


Fig. 3. Results of deuterolysis of chromium reduced with LiNp.

The amount of ^1H evolved per metal atom also slightly increases with increasing ratio LiNp/M. The limiting value, however, seems to be two in the cases of V and Cr, and one for Ni. It is remarkable that with Ni, at LiNp/Ni = 2.1, one ^1H per atom is essentially the only gas evolved on reaction with ^2H_2O.

The evolved ^1H clearly cannot originate from the heavy water, and thus evidences the presence of metal–hydrogen bonds. The isotope distribution furthermore indicates the hydrogen to be bonded to the metal in a form which allows a free radical release, since only in this way does the relatively high percentage of $^1H_2$ observed in some of the experiments become understandable. (The polar LiH, *e.g.*, would yield quantitatively $^1H^2H$, and no $^1H_2$, on deuterolysis; see *Experimental*).

In all experiments with nickel, using normal as well as heavy water, the metal precipitates in form of Ni(0) sponge. If dilute HCl is used for the hydrolysis, soluble Ni(II) is obtained, and roughly one H_2 more per Ni atom is evolved, as shown in Table 2 (ΔH_2/Ni).

TABLE 2

HYDROGEN EVOLUTION FROM REDUCED NICKEL SOLUTIONS, WITH WATER AND DILUTE HCl RESPECTIVELY

LiNp/Ni	*H_2/Ni*		*ΔH_2/Ni*
	with H_2O	*with HCl*	
3	0.82	2.00	1.18
7	1.50	2.80	1.30
19	3.00	3.75	0.75

From these results it can be concluded that nickel, in the LiNp reduced solutions, is present as Ni(0) (or as a negatively charged species) but not as Ni(I) or Ni(II). Further evidence for the presence of Ni as Ni(0), at LiNp/Ni = 2.1, was obtained on reacting such solution with tetramethylcyclobutene dibromide and obtaining quantitatively (referred to Ni) the tetramethylcyclobutadiene complex with Ni(II)[4].

Vanadium and chromium, on the other hand, do not precipitate as M(0) on hydrolysis, nor show differences between H_2O and HCl with respect to the volume of hydrogen evolved. If the hydrolysis of the reduced vanadium solutions is carried out under careful exclusion of oxygen, the violet color of V(II) can be observed. The hydrolysis of Cr solutions yield liquids presenting a yellow-brown color. For reasons discussed below it is assumed that Cr(II) is formed. These findings are, however, not in contradiction to the presence of M(0), or negatively charged species, in the original solutions, since V(0) and Cr(0), contrary to Ni(0), should decompose water, due to their higher oxidation potentials.

(*b*) *Electron paramagnetic resonance*

The vanadium species are especially attractive for EPR investigation, due to the magnetic nucleus of ^{51}V ($I = 7/2$) and to the fact that V(0) possesses one unpaired electron.

At a ratio of LiNp/V = 3 which, starting from V(III) salts, corresponds to the stoichiometric amount of reducing agent for the reduction V(III)→V(0), one observes a relatively strong signal which is represented in Fig. 4. The spectrum shows an eight line hyperfine splitting (HFS) due to the ^{51}V nucleus; each line is furthermore split into an odd number of lines. The spectroscopic constants of this spectrum ($g = 1.962$, $a_V = 63$ gauss, $a_H = 3.9$ gauss) show convincing concordance with the spectra of bis-arene-V (0) complexes ("sandwich complexes") which have been recently described for benzene, toluene and mesitylene[5,6]. Thus the additional HFS shows unambiguously the interaction of the unpaired electron of the vanadium with hydrogen nuclei of two naphthalene molecules, and it can be concluded that at least part of the metal is present as bis-naphthalene-V(0).

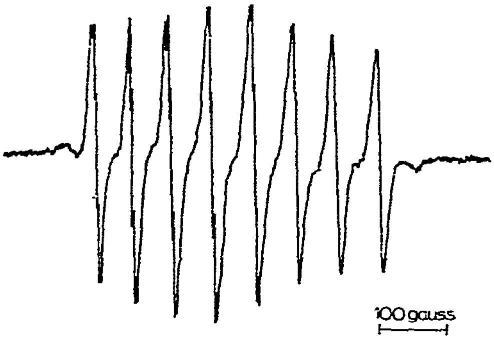


Fig. 4. EPR signal of vanadium reduced with LiNp at LiNp/V = 3.

At higher ratios LiNp/V this EPR signal weakens; at LiNp/V ≥4 it is practically absent. A reasonable explanation for this observation would be a further electron transfer from naphthalide anions to the V(0) complex, providing a pairing of the so far unpaired electron.

At 5≤ LiNp/V ≥6 a new, although relatively weak, 8 line vanadium spectrum is observed which presents a considerably smaller ^{51}V HFS constant, $a_V = 58$ gauss.

(No hydrogen HFS can be observed, possibly due to the low signal-to-noise ratio of the weak signal.) Following the so far observed trend of the ^{51}V HFS constants, *i.e.* V(IV): $a_V = 114$ gauss[7,8]; V(II): $a_V = 93$ gauss[8]; V(0): $a_V = 63$ gauss[5,6], it seems plausible to suppose a V(−II) species to be responsible for the $a_V = 58$ gauss pattern. (The intermediate species V(III), V(I), etc., are not EPR active.)

From these observations it follows that LiNp, in excess to the stoichiometric amount for the reduction V(III)→V(0), is used up for further reduction of the complex. This is in agreement with the fact that the EPR signal of LiNp ($g = 2.00$) cannot be observed at $LiNp/V < 6$. This last statement is also valid for the chromium case, and, with a value of $LiNp/Ni < 5$ also for the Ni case.

DISCUSSION

The hydrolysis experiments have shown that with increasing ratio LiNp/M, an increasing amount of hydrogen is evolved. The use of heavy water led to the conclusion that with the exception of 1–2 hydrogen atoms per metal atom, the gas proceeds from the decomposition of water.

Free LiNp reacts with water without appreciable hydrogen evolution since the compound incorporates the hydrogen according to[9]:

$$2\,LiNp + 2\,H_2O \longrightarrow 2\,LiOH + Np + NpH_2$$

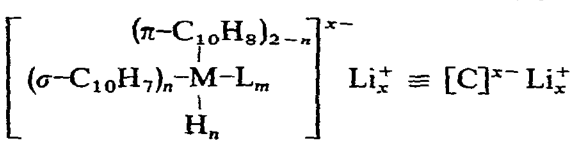
$$(Np = \text{naphthalene};\ NpH_2 = \text{dihydronaphthalene})$$

Thus the increasing number of electrons necessary for the decomposition of water, although evidently originating from the LiNp, must be stored in some way, most probably within the confines of transition metal complexes.

On the other hand, the EPR measurements indicate these metal complexes to be, at least partially, of the bis-arene type. EPR data also confirm the disappearance of a considerable amount of excess LiNp.

The results concerning the ^1H content are probably best interpreted by assuming the reduced metal to be capable of abstracting hydrogen from complexed naphthalene molecules, in a manner similar to that described by Chatt and Davidson[10] for the ditertiary phosphine stabilized complex of Ru(0) with naphthalene. A certain mobility of hydrogen atoms in ligands of transition metal complexes with filled *d*-shells has repeatedly been reported (see the cited paper of Chatt *et al.*[10], and references therein). Undoubtedly, however, C–H bonds in the ligands of bis-arene-V(0) and bis-arene-Cr(I) complexes are also influenced by the presence of the metal, as shown by EPR evidence[6].

Thus the experimental data suggest that the LiNp reduced metals are present as complexes which may be formulated, in a very general manner, as:



$$\left[\begin{array}{c} (\pi\text{-}C_{10}H_8)_{2-n} \\ | \\ (\sigma\text{-}C_{10}H_7)_n\text{-}M\text{-}L_m \\ | \\ H_n \end{array}\right]^{x-} Li_x^+ \equiv [C]^{x-}\,Li_x^+$$

(x = number of negative charges, increasing with increasing excess of LiNp; $n = 1$ or 2; L = solvent ligand; m = number of solvent ligands necessary to satisfy the symmetry requirements of the corresponding metal).

Most probably several species with varying x are in equilibrium and there might exist also an equilibrium with the corresponding bis-arene complexes ($n = 0$).

Some of the experiments of Table 1 may now be discussed in more detail, in the light of the proposed complex structure.

The nickel complex at LiNp/Ni = 2.1 can be envisaged with $n = 1$ and $x = 0$. One hydrogen is ejected, on deuterolysis, as a radical which combines with another $^1H^{\cdot}$ to give $^1H_2$. No extra charge is present, since roughly the stoichiometric amount of LiNp for the reduction Ni(II)→Ni(0) has been used. Furthermore Ni(0) is not able to decompose the heavy water. Thus no ^2H at all is evolved.

The heavy water has sort of a catalytic effect in this process, in the sense that it is not changed in the reaction. Presumably it acts in a first phase of the process displacing certain, or all, of the ligands around the nickel atom. However Ni(0) is not maintained in solution in this new environment, but precipitates as metal sponge. The process may be formulated as:

$$[C]^0(+{}^2H_2O) \rightarrow M(0) \times {}^1H^{\cdot} + C_{10}H_7^{\cdot} + m\,L(+{}^2H_2O) \qquad (1)$$

The naphthyl group must also be liberated as a radical which probably abstracts hydrogen from the solvent to give again naphthalene.

In the corresponding chromium experiments (at LiNp/Cr = 3.3) the situation is somewhat different. Since about one $^1H^{\cdot}$ per Cr is liberated on deuterolysis it is also $n = 1$. Again the complex has no extra charge ($x = 0$), since roughly the stoichiometric amount of LiNp for Cr(III)→Cr(0) has been added. Nevertheless two deuterium radicals per chromium atom are evolved (exactly 1.92, see column 8 in Table 1). This finding can easily be understood as a decomposition of the heavy water by Cr(0). Since $^2H/Cr \simeq 2$, it is plausible to assume that the oxidation of the chromium reaches only the state Cr(II) (at least in the time of observation, 30 minutes). Thus the evolution of $^2H^{\cdot}$ can be formulated in this case:

$$Cr(0) + 2\,{}^2H_2O \rightarrow Cr(O^2H)_2 + 2\,{}^2H^{\cdot} \qquad (2)$$

Obviously, however, the two types of radicals, $^1H^{\cdot}$ and $^2H^{\cdot}$, are not liberated simultaneously. This follows from the experimental isotope distribution given in Table 1 (columns 3–5), as compared with the theoretical distribution expected if the radicals

TABLE 3

THEORETICAL ISOTOPE DISTRIBUTION EXPECTED FOR STATISTICAL COMBINATION OF $^1H^{\cdot}$ AND $^2H^{\cdot}$ (REFER TO EXPERIMENTS IN TABLE 1)

Metal salt	*LiNp/M*	*$^1H_2$ (%)*	*$^1H^2H$ (%)*	*$^2H_2$ (%)*
VCl_3	3.1	16.0	48.0	36.0
	25.0	3.3	29.5	67.2
$CrCl_3$	3.3	13.0	45.8	41.2
	6.3	4.7	34.3	61.0
	10.0	2.8	28.4	68.8
	25.0	3.6	30.7	65.7
$NiBr_2$	2.1	100	0	0
	5.0	16.8	48.2	35.0
	30.0	2.0	24.0	74.0

were present simultaneously and could combine in a statistical manner. This latter distribution is given in Table 3 for the experiments cited in Table 1. [If α = atom fraction of $^1H^\bullet$, then $\alpha^2 = {}^1H_2$, $(1-\alpha)^2 = {}^2H_2$ and $2\alpha(1-\alpha) = {}^1H^2H$][10].

From the data found for the chromium case at LiNp/Cr = 3.3 it follows that by far more $^1H_2$ and $^2H_2$ are observed experimentally (Table 1) than expected for statistical combination (Table 2). Presumably reaction (2) occurs considerably more slowly than reaction (1), thus giving rise to the evolution of most of the $^1H^\bullet$ at an earlier time than to the evolution of most of the $^2H^\bullet$. The same effect can also be observed in the vanadium experiment at LiNp/V = 3.1.

At higher ratios of LiNp/M two phenomena can be observed. On the one hand an increasing amount of ^2H is found at increasing LiNp/M. Extra charges of the complex must be responsible for this additional decomposition of the heavy water, according to:

$$[C]^{x-}Li_x^+ + x\,{}^2H_2O \rightarrow [C]^0 + x\,LiO^2H + x\,{}^2H^\bullet \qquad (3)$$

From the experiments shown in Fig. 3 it can be concluded that these extra charges, in the case of Cr, are limited to a value of six per metal atom [taking into account that two $^2H^\bullet$ per chromium are evolved according to reaction (2)]. As indicated above, it can be assumed that vanadium shows a very similar behavior. Also in the nickel case, where all of the observed ^2H has to be attributed to reaction 3, the limiting value appears to be six. This astonishing agreement of the number of possible charges to be incorporated per metal unit, independent of the metal considered, suggests that these extra electrons are essentially delocalized on the ligands.

On the other hand the evolution of ^1H increases slowly, although only in the cases of Cr and V. Two $^1H^\bullet$ per metal atom seems to be the limiting value, which would correspond to a value of $n = 2$ in the formula given above for the complexes. This finding seems to indicate that the higher charged complexes of V and Cr contain the metal in a form which enables a further hydrogen abstraction from naphthalene.

A further observation seems to be significant. Whereas Cr and V tend to an asymptotic value of 2 $^1H^\bullet$/M, at high LiNp/M, the nickel complexes evolve only 1 $^1H^\bullet$ per nickel atom at any ratio LiNp/Ni. It is believed that this fact, contrary to the number of electrons admitted per metal unit, is an intrinsic property of the metal which should probably be attributed to the *d*-population.

Finally it should be noted that at higher LiNp/M the discrepancy between the experimental isotope distribution and the calculated one for the case of simultaneous presence and statistical combination of $^1H^\bullet$ and $^2H^\bullet$ decreases markedly. This seems to show that the $^1H^\bullet$ proceeding from the reaction 1 and the $^2H^\bullet$ from reaction 3, have a sufficiently long common lifetime for statistical combination.

EXPERIMENTAL

Solutions of reduced transition metals have been prepared adding the metal salt dissolved in THF ([M-salt] = 10^{-2}–10^{-3} mol/l), in argon countercurrent to the LiNp solution in THF ([LiNp] = 10^{-1}–10^{-2} mol/l).

The reduced solutions have been injected with a medical syringe, provided with a bent needle, into a gas buret filled with oxygen-free water. The measured gas volume was corrected for temperature and pressure, as well as for the vapor pressure of the water and the injected THF. Blank experiments have been carried out with LiNp. In agreement with Coates[9] an extremely week gas evolution was observed which amounted, on the average, to $H_2/LiNp = 0.02$. Only in cases of $LiNp/M > 10$ have the measured values been corrected for this hydrogen evolution.

Mass spectra were obtained with a "time of flight" mass spectrometer (Bendix), using ^2H_2O (FLUKA AG) for the decomposition of the reaction solutions. LiH was used as test substance. $\geqslant 97\%$ of the gas evolved was $^1H^2H$, indicating a relatively high isotopic purity of the heavy water.

Exchange between ^2H from the gas phase and ^1H from the reactants was checked in the following way. $^2H_2$ was prepared from the heavy water and metallic lithium. This gas was maintained in contact with THF, naphthalene in THF, and LiNp in THF respectively, during 24 hours. Mass spectroscopic analysis showed in all three cases the same isotope distribution as in the original $^2H_2$.

A Varian V-4502 Spectrometer with 100 kc field modulation was used for the EPR measurements. The characteristic parameters (g-value, a_V, a_H) have been obtained by comparison with a standard sample of peroxylaminodisulphonate ($g = 2.0055$; $a_N = 13.0 \pm 1$ gauss).

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SUMMARY

EPR spectroscopical evidence is presented for the formation of arene complexes during the reduction of transition metal salts with lithium-naphthalide in tetrahydrofuran. Deuterolysis of such solutions demonstrates an intramolecular hydrogen transfer from naphthalene to metal. Up to 6 negative charges per metal atom can be incorporated by such arene complexes.

REFERENCES

1 T. L. CHU AND J. V. FRIEL, *J. Am. Chem. Soc.*, 77 (1955) 5838.
2 G. HENRICI-OLIVÉ AND S. OLIVÉ, *Chimia*, 19 (1965) 46.
3 G. HENRICI-OLIVÉ AND S. OLIVÉ, *Makromol. Chem.*, 88 (1965) 117.
4 G. HENRICI-OLIVÉ AND S. OLIVÉ, to be published.
5 K. H. HAUSSER, *Z. Naturforsch.*, 16a (1961) 1190.
6 G. HENRICI-OLIVÉ AND S. OLIVÉ, *Z. Physik. Chem. NF*, in press.
7 G. NATTA, A. ZAMBELLI, G. LANZI, I. PASQUON, E. R. MAGNASCHI, A. L. SEGRE AND P. CENTOLA, *Makromol. Chem.*, 81 (1965) 161.
8 G. HENRICI-OLIVÉ AND S. OLIVÉ, unpublished results.
9 G. E. COATES, *Organo-Metallic Compounds*, Methuen, London, 1960.
10 J. CHATT AND J. M. DAVIDSON, *J. Chem. Soc.*, (1965) 843.