Polyhedron Vol. 10, No. 23/24, pp. 2827–2832, 1991
Printed in Great Britain

0277–5387/91 $3.00+.00

THE CYCLIC FIXATION AND REDUCTION OF MOLECULAR NITROGEN WITH [$WH_4(Ph_2PCH_2CH_2PPh_2)_2$] IN γ-IRRADIATED SOLUTIONS

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(*Received* 19 *April* 1991; *accepted* 2 *July* 1991)

Abstract—Yields of NH_3 and N_2H_4 in radiation-catalytic reduction of N_2 by means of a hydride complex of W^{IV} with dppe in thf solution and in mixtures of thf with other solvents have been estimated. A mechanism proposed earlier of reduction of coordinated N_2 has been confirmed and the role of solvent in reduction of N_2 to NH_3 and amines has been explained.

In our recent work it has been shown that the hydride complexes of W^{IV} and Mo^{IV} with $Ph_2PCH_2CH_2PPh_2$(dppe) have higher activity as catalysts in the process of radiation-catalytic reduction of molecular nitrogen when compared with the activity of [MoOCl(dppe)$_2$] and [M(dppe)$_2$] (M = Mo, W).[1-4]

Making a comparison between the yields of the redox factors (i.e. H, e_s^-, R) and the yields of H_4N_2 and H_3N it was pointed out that the corresponding complexes formed H^- ions as a result of attachment of H^+ ions to the central ions,[5] and the H^- ions formed could reduce the coordinated N_2.

Using [WH_4(dppe)$_2$] as a catalyst revealed the formation of [$WH(N_2)_2$(dppe)$_2$]$^+$ ions and their reduction to H_4N_2 in a radical process (by means of H atoms from [WH_5(dppe)$_2$]$^+$ and then to H_3N in an ion involved process (with H^- ions and e^- from the central ion).[2]

In our previous work[2] the remarkable effect of the solvent on the yields of H_3N was shown—the more stable the W—H group the higher the yields of ammonia in the particular solvent.

It is apparent that the role of the solvent cannot be restricted to the thermodynamic aspects of the M—H groups. Especially in the radiation process features such as molecular structure, polarity and polarizability, not to mention the donor–acceptor abilities of the solvent, play a very important role parallel to the stable and unstable radiolysis products.

The influence of the solvent on the yields and the products of the chemical reduction of coordinated N_2 has been reported,[6,7] but not explained so far. Thus, the problem of the solvent choice in the process of nitrogen fixation, especially for a cyclic process in a γ-radiation field is still to be explored. Taking into account the poor solubility of the neutral and ionic complexes of W^{IV} and Mo^{IV} on the one hand and thermodynamic and kinetic properties of the complex solutions including the yields of the stable and unstable radiolysis products on the other, we decided to use tetrahydrofuran (thf) and its mixtures as the most proper solvents. Thf is a medium polarity solvent and the products of its radiolysis are similar to those of the previously applied solvents, i.e. alcohols and cyclohexane.[8] In a mixture of thf with cyclohexane the yields of H_3N are supposed to be higher, while a small addition of water as a polar component can lead to the lower yields of N_2 reduction. The latter suggestion could support the results of our earlier works.

The application of the higher doses is accompanied by a lowering of the yields of ammonia in the solutions of Mo^{IV} and W^{IV} complexes. That fact is to be explained in this paper.

EXPERIMENTAL

Ligand dppe and a complex [WH_4(dppe)$_2$] were synthesized according to the literature.[9] Thf was

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purified by refluxing with $LiAlH_4$ and then distilled. Before making solutions, thf and its mixtures with cyclohexane were saturated with N_2+H_2 mixtures or deoxygenated nitrogen.

The complex was dissolved in thf or its mixtures with cyclohexane. The solutions of $[WH_5(dppe)_2]HSO_4$ were obtained by the dissolving of $[WH_4(dppe)_2]$ in 0.1 M or 0.01 M solutions of H_2SO_4 in thf, thf+cyclohexane or thf+H_2O. The solutions of $[WH_5(dppe)_2]HSO_4$ were irradiated in a γ-radiation ^{60}Co source (Issliedowatiel) with simultaneous saturation of the proper solution with deoxygenated nitrogen or a mixture of deoxygenated nitrogen and hydrogen (v/v = 1 : 3). Dose rate was calculated as 7.66×10^{16} eV cm^{-3} min^{-1} in conversion to thf solution on the basis of a Fricke's dosimeter. In order to keep the concentrations of the solutions constant the gases were passed through the scrubbers filled with the proper solvent.

The H_4N_2 and H_3N generated were absorbed in aqueous solutions of H_2SO_4 ($c = 5 \times 10^{-2}$ M). Hydrazine and ammonia were determined by the standard methods, according to the cited papers,[9,10] respectively. For the acidified solutions the products were estimated in the irradiated solutions and in the traps filled with sulphuric acid using the same procedure. The aliphatic amines were detected spectrophotometrically, using salicyl aldehyde.[13] IR spectra were recorded for the irradiated solutions or in KBr pellets (the latter for the substances isolated from the irradiated solutions after evaporation of the solvent). The spectra were made using a Specord 75 IR spectrophotometer. ^{1}H and ^{31}P NMR spectra were made using a VXR-300 Varian spectrometer. The resonance signals were measured in the irradiated solutions and for the substances isolated from the irradiated solutions. Such substances were dissolved in $CDCl_3$.

RESULTS AND DISCUSSION

The numbers of $(N_2H_6)SO_4$ ions are shown in Fig. 1 and the numbers of $(NH_4)_2SO_4$ molecules in Fig. 2 vs dose and the concentrations of $[WH_5(dppe)_2]^+$ solutions. The radiation yields of ammonia and hydrazine together with the catalytic efficiency of the N_2 reduction are presented in Table 1. The catalytic efficiency of the process equals the number of NH_4^+ ions formed during 1 h irradiation of the $[WH_5(dppe)_2]HSO_4$ solutions. The number of ions is related to 1 mol of $[WH_5(dppe)_2]^+$ ions. Since, according to our earlier work,[2] only 1/3 of the complex is engaged in fixation of N_2, the numbers in column 5 were tripled.

The curves in Fig. 1 are similar to those presented in our earlier papers[1-5] where different complexes and solvents were applied and the shapes of the curves were explained earlier.[4] The apparent formation of ammonia as a result of reduction of hydrazine was elaborated earlier.[1-5] It is easy to notice from Table 1 and Figs 1 and 2 that the radiation yields of ammonia and hydrazine do not depend directly on the concentrations of the complex. The relative catalytic efficiency (excluding the formation of the W—H groups, H_4N_2 and RNH_2) is increased at the lower concentrations of $[WH_4(dppe)_2]$ and the opposite effect is observed at the higher concentrations. The results presented are likely to be due to the too low dose rate applied. As a consequence, too many molecules of the catalyst

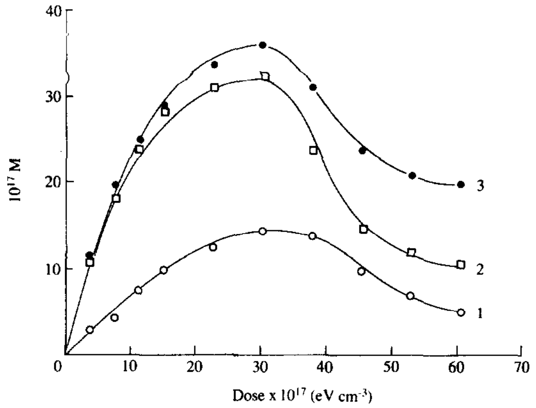


Fig. 1. The numbers of $(N_2H_6)SO_4$ molecules per 1 cm^3 (M) vs dose and concentration of a catalyst in acidified thf solution saturated with N_2+H_2 (1 : 3) mixture. Conc. $[WH_4(dppe)_2]$ = (1, ○) 5×10^{-3} mol dm^{-3}; (2, □) 1×10^{-2} mol dm^{-3}; (3, ●) 5×10^{-2} mol dm^{-3}.

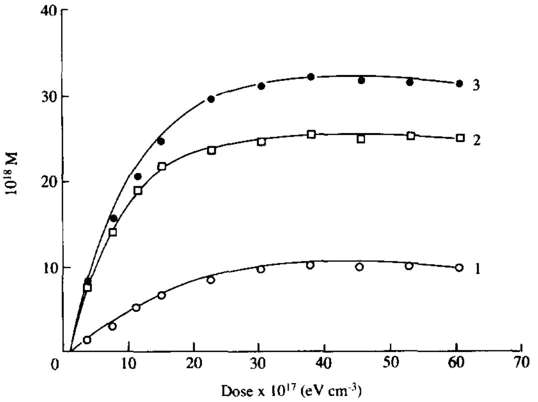


Fig. 2. The numbers of $(NH_4)_2SO_4$ molecules per 1 cm^3 (M) vs dose and concentration of a catalyst in acidified thf solution saturated with N_2+H_2 (1 : 3) mixture. Conc. $[WH_4(dppe)_2]$ = (1, ○) 5×10^{-3} mol dm^{-3}; (2, □) 1×10^{-2} mol dm^{-3}; (3, ●) 5×10^{-2} mol dm^{-3}.

Table 1. The parameters of the catalytic system ([$WH_4(dppe)_2$] dissolved in thf acidified with H_2SO_4 saturated with N_2+H_2)

Concentration of [$WH_4(dppe)_2$] (mol dm^{-3})	Number of $N_2H_6^{2+}$ ions/100 eV	Number of NH_4^+ ions/100 eV	Concentration of NH_4^+ ions after absorption of dose 45.36×10^{17} eV cm^{-3} (mol dm^{-3})	NH_4^+/[$WH_4(dppe)_2$] fixing N_2
5×10^{-3}	77	687	1.67×10^{-2}	10
1×10^{-2}	214	4174	4.24×10^{-2}	13
5×10^{-2}	317	5700	5.29×10^{-2}	3.3

do not take part in the process of fixation and reduction of N_2. The visible induction period (see Figs 2, 4 and 5) was explained earlier.[1-5] The yields of N_2 reduction in the presence of $[WH_5(dppe)_2]^+$ in thf are higher than those in cyclohexane–ethanol and cyclohexane–methanol systems.[2] Our earlier hypothesis that the higher stability of the hydride complex in a low polarity solvent can effect the yields of hydrazine and ammonia seems to be supported by that observation. However, in thf solutions the numbers of NH_4^+ are slightly decreased while increasing the dose as for methanol and methanol–cyclohexane systems.[2,3-5] The observed decrease of the NH_4^+ concentrations was explained earlier[3] as a result of their reactions with the radicals formed in the course of radiolysis of methanol. In the irradiated thf solutions the radicals formed, C_4H_7O,[8,14] can react with NH_4^+ ions and H_3N molecules. It is obvious for the reaction (1) type to go independently of the dose in the γ-radiation field, however in the initial stage of N_2 reduction its rate is much lower than that of the H_3N formation. That is why an increase of the NH_4^+ ions concentration is observed until the plateau starts (see Fig. 2).

$$H_3N + R \longrightarrow RH + NH_2 \quad \text{(ref. 3)}. \qquad (1)$$

When the plateau starts, the rate of reaction (1) is greater than the rate of H_3N formation. Thus, the application of greater doses is accompanied by a decrease in the number of NH_4^+ ions. The rate of coordinated nitrogen reduction to ammonia is affected by a concentration of H^- ions.[1,2] The ions can be formed as a result either of the substitution of W—N_2 groups by W—H group or addition of H^+ ions into the central atom.

The equal tangents of the curves from Figs 3 and 4 for the acidified solutions saturated with nitrogen and the non-acidified ones saturated with nitrogen–hydrogen mixture, and, as a consequence, the equal values of $G_{NH_4^+}$ are satisfying supports for the previously proposed two ways of formation of H^- ions and their influence on the reduction of N_2. Regardless of the way H^- ions are formed, they possess the same ability to reduce H_4N_2 to H_3N, i.e. at different oxidation states of the central W ions the $G_{NH_4^+}$ values are equal in the acidified solutions saturated with nitrogen and in the non-acidified ones saturated with nitrogen–hydrogen mixture (see Fig. 4 and Table 2). The association of H^+ ions to W ions is a very rapid process when compared with the process of H^- ion formation to be a result of N_2 elimination using H_2. Therefore, the amount of hydrazine to be reduced to NH_4^+ ions is the lowest in the non-acidified solutions (see Figs 3 and 4). Insufficient concentration of the H^- ions prevents the reduction of all the hydrazine to ammonia (high placed plateau in curve 1 in Fig. 3). Thus, as a consequence, the $G_{NH_4^+}$ in non-acidified solutions is lower than that in the acidified ones and/or solutions saturated with hydrogen (Fig. 4 and Table 2). Hence, the influence of hydrazine amount on the yields of ammonia is supported and the role of H^- and H^+ ions in the process of reduction of molecular nitrogen seems to be explained sat-

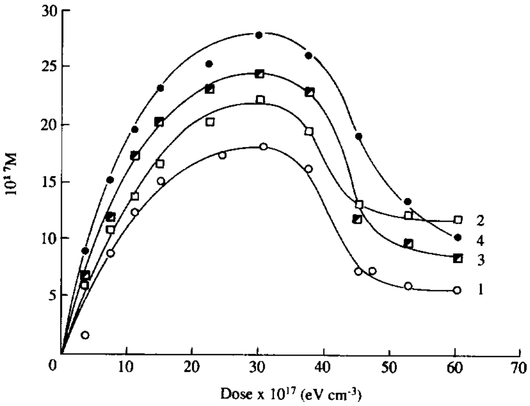


Fig. 3. The numbers of $(N_2H_6)SO_4$ molecules per 1 cm^3 (M) vs dose and concentration of H_2SO_4 (c[$WH_4(dppe)_2$] = 1×10^{-2} mol dm^{-3}) in thf solution. $c_{H_2SO_4}$ = (1) 0 mol dm^{-3} (○)—saturated with N_2+H_2 (1 : 3); (2) 10^{-2} mol dm^{-3} (□)—saturated with N_2; (3) 10^{-1} mol dm^{-3} (◪)—saturated with N_2; (4) 10^{-2} mol dm^{-3} (●)—saturated with N_2+H_2 (1 : 3).

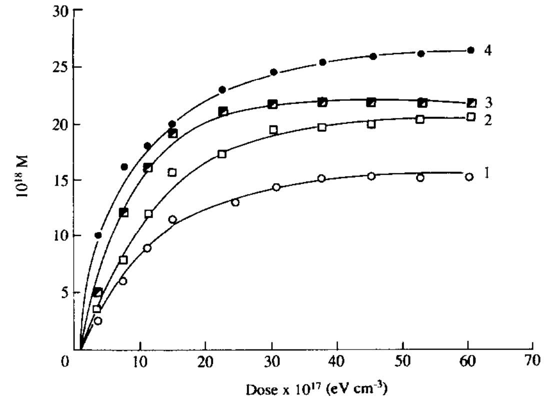


Fig. 4. The numbers of $(NH_4)_2SO_4$ molecules per 1 cm^3 (M) vs dose and concentration of H_2SO_4 (c[$WH_4(dppe)_2$] = 1×10^{-2} mol dm^{-3}) in thf solution. $c_{H_2SO_4}$ = (1) 0 mol dm^{-3} (○)—saturated with N_2+H_2 (1 : 3); (2) 10^{-2} mol dm^{-3} (□)—saturated with N_2; (3) 10^{-1} mol dm^{-3} (◪)—saturated with N_2; (4) 10^{-2} mol dm^{-3} (●)—saturated with N_2+H_2 (1 : 3).

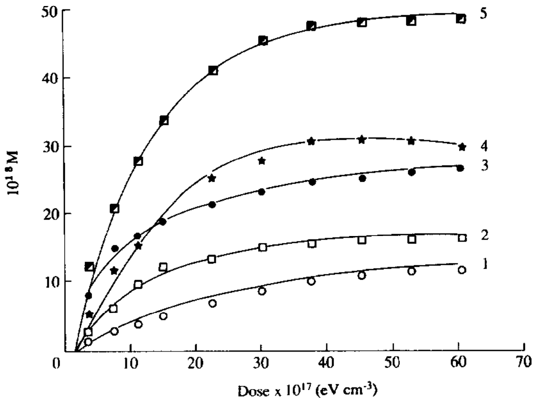


Fig. 5. The numbers of NH_4^+ ions per 1 cm^3 (M) vs dose and concentration of [$WH_4(dppe)_2$] in different systems. (1,○) c[$WH_4(dppe_2)$] = 5×10^{-3} mol dm^{-3} in thf+dppe (c = 5×10^{-3} mol dm^{-3}) saturated N_2+H_2 (1 : 3); (2, □) c[$WH_4(dppe)_2$] = 1×10^{-2} mol dm^{-3} in thf+dppe (c = 1×10^{-2} mol dm^{-3}) saturated N_2+H_2 (1 : 3); (3, ●) c[$WH_4(dppe)_2$] = 1×10^{-2} mol dm^{-3} in thf acidified+dppe (c = 1×10^{-2} mol dm^{-3}) saturated N_2+H_2 (1 : 3); (4, ★) c[$WH_4(dppe)_2$] = 1×10^{-2} mol dm^{-3} in thf+C_6H_{12} (1 : 1) saturated N_2+H_2 (1 : 3); (5, ◪) c[$WH_4(dppe)_2$] = 1×10^{-2} mol dm^{-3} in thf acidified+C_6H_{12}(1 : 1)+dppe (c = 1×10^{-2} mol dm^{-3}) saturated N_2+H_2 (1 : 3).

isfactorily. Nevertheless, the H^+ ions could protonate the coordinated nitrogen and, indirectly, the other products of reduction. The influence of H^- ions on the mechanism of N_2 reduction (i.e. disproportionation of —NNH_2 group) was observed by the other authors.[15] The influence of the solvent on the coordination sphere of the catalyst is thought to be another reason for the decreasing rate of formation of H_3N when the applied dose is increased.

When free ligand dppe is present in the reaction system it affects the yields of H_4N_2; either in the acidified solutions or in the non-acidified ones the yield of hydrazine is increased about 20% while the yield of NH_4^+ ions is increased about 20% in the acidified solutions only (compare curves 1 and 2 in Fig. 5 with curve 1 in Fig. 4 and the corresponding data from Tables 1–3). The curves in Fig. 5 (excluding curve 4) have permanent tendencies to increase their values, however, at the higher doses the rate of ammonia formation is distinctly lower than at the initial stage of the process. In the non-acidified solutions the presence of dppe does not affect G_{NH_3}, however, due to the relatively high value of $G_{N_2H_4}$ the concentration of NH_3 is increased. These observations suggest that dppe is liberated from the coordination sphere in the two-step competitive pathway (2 and 3) which is as

Table 2. The parameters of the catalytic system (c[$WH_4(dppe)_2$] = 10^{-2} mol dm^{-3})

Concentration of H_2SO_4 (mol dm^{-3})	Satur. gas	Number of $N_2H_6^{2+}$ ions/100 eV	Number of NH_4^+ ions/100 eV	Concentration of NH_4^+ ions after absorption of dose 45.36×10^{17} eV cm^{-3} (mol dm^{-3})	NH_4^+/[$WH_4(dppe)_2$] fixation N_2
1×10^{-2}	N_2	141	1218	3.17×10^{-2}	9.6
1×10^{-1}	N_2	176	3130	3.49×10^{-2}	10.6
1×10^{-2}	N_2+H_2 (1 : 3)	212	3826	3.79×10^{-2}	11.5
0	N_2+H_2 (1 : 3)	132	1217	2.52×10^{-2}	7.6

Table 3. The parameters of the catalytic system (complex solution ($c = 1\times10^{-2}$ or 5×10^{-3}* mol dm^{-3}) saturated with N_2+H_2)

Irradiated system	I	II	III	IV
Conc.* in thf acidified + dppe ($c = 5\times10^{-3}$ mol dm^{-3})	93	800	1.81×10^{-2}	11.3
Conc. in thf acidified + dppe ($c = 1\times10^{-2}$ mol dm^{-3})	282	4400	2.53×10^{-2}	7.7
Conc. in thf + dppe ($c = 1\times10^{-2}$ mol dm^{-3})	159	1217	2.69×10^{-2}	8.1
Conc. in thf$-C_6H_{12}$ (1 : 1)	182	2700	5.17×10^{-2}	15.7
Conc. in thf acidified + C_6H_{12} (1 : 1) + dppe ($c = 1\times10^{-2}$ mol dm^{-3})	388	8380	7.92×10^{-2}	24.0
Conc. in thf acidified + H_2O (1 : 1)	11	200	1.04×10^{-2}	3.0
Conc. in thf + C_6H_{12} (1 : 1)	78	NH_4^+ 800 RNH_2 116	NH_4^+ 3.53×10^{-2} RNH_2 10.4×10^{-3}	NH_4^+ 21.2 RNH_2 2.74

I—numbers of $(N_2H_6)SO_4$ molecules per 100 eV.
II—numbers of $(NH_4)_2SO_4$ or RNH_2 molecules per 100 eV.
III—concentrations of NH_4^+ ions or RNH_2 molecules after absorption of 45.36×10^{17} eV cm^{-3} (mol dm^{-3}).
IV—numbers of NH_4^+ ions or RNH_2 molecules per number of $[WH_4(dppe)_2]$ moles fixing N_2.

follows:

$$[\mathrm{WH(N_2)_2(dppe)_2}]^+ + [\mathrm{WH_5(dppe)_2}]^+ + 2\,\mathrm{HSO_4^-} \rightarrow [\mathrm{HWNNH_2(SO_4)(dppe)}]^+ + \mathrm{N_2} + [\mathrm{WH_3(dppe)_2}]^+ + (\mathrm{dppe\,H_2})\mathrm{SO_4} \qquad (2)$$

$$[\mathrm{HWNNH_2(SO_4)(dppe)}]^+ \xrightarrow[\mathrm{dppe\,H_2^{2+}}]{\mathrm{2thf,\,2H}} \begin{cases} \xrightarrow{a} [\mathrm{HW(N_2H_4)(thf)_2(dppe)}]^+ + \mathrm{SO_4^{-2}} \\ \xrightarrow{b} [\mathrm{HW(N_2H_4)(dppe)_2}]^+ + \mathrm{H_2SO_4} \end{cases} \qquad (3)$$

The products of reaction (2) were not isolated due to their instability and relatively low concentration. The composition of the $[\mathrm{HWNNH_2(SO_4)(dppe)}]^+$ product was proposed as the most likely one.

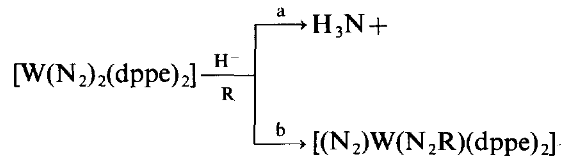
The formation of the hydrazide complexes of type $[\mathrm{WNNH_2(HSO_4)_2L_3}]$ was shown by other authors.[16] Since the central ion is protonated the HSO_4^- ion is most likely to act as a bidentate ligand (in a form of SO_4^{2-} ion).[17]

Reactions (2) and (3) are complementary to those presented earlier when $[\mathrm{WH_5(dppe)_2}]^+$ was applied as a catalyst.[2] For a process made in thf-cyclohexane system the role of reaction 3a is slightly diminished. The effect is enlarged by the small addition of dppe into the reaction system. The latter is accompanied by the apparent increase of the yields of NH_4^+ ions. On the other hand, the addition of a polar solvent (i.e. H_2O) into thf solution results in a contradictory effect of decreasing yields of hydrazine and ammonia.

The liberation of dppe from the coordination sphere of the complex was monitored by ^{31}P NMR spectroscopy. In a solution of $[\mathrm{WH_4(dppe)_2}]$ in thf ($c = 1\times10^{-2}$ M) irradiated with a dose 5.4×10^{18} eV cm^{-3} two signals at 33.44 and 27.02 ppm were observed. The former was attributed to $[\mathrm{WH_x(dppe)_2}]$ ($x < 4$)[18] complex while the latter was assigned to phosphine oxide[19] which is formed as a result of a liberation of dppe from the coordination sphere of the complex and its oxygenation by oxygen from the air. The chemical shifts of ^{31}P signals of dppe and its oxide were determined for the non-irradiated samples as -12.13 and 27.02 ppm, respectively.[19b] Comparing the integral intensities of the ^{31}P signals one could count the amount of dppe which is effectively exchanged by thf in the coordination sphere to be 10% of the whole amount of the former. Thus, reactions 2 and 3a could not be assumed to have decreased the rate of N_2 reduction to H_3N.

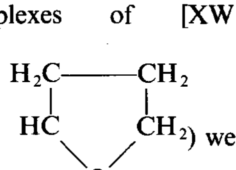
That conclusion seems to be supported by the fact of a relatively high concentration of the bis-dinitrogen complex of W in the irradiated complex solution. In fact, in the IR spectrum of the complex a few characteristic bands appear, e.g. at 1960 cm^{-1} assigned as A_{2u} vibration of a $W(N_2)_2$ group, besides, the lower intensities of the bands at 1830, 1775 and 1730 cm^{-1} attributed to ν(W—H) vibrations are due to the lower concentration of W—H groups in the irradiated solution of $[WH_4(dppe)_2]$. Thus, the other direction of the process of dinitrogen reduction leading neither to hydrazine nor to ammonia could be taken into account. The reduction by the radicals with the simultaneous action of H^+ or H^- ions and H atoms seems to be the alternative explanation of the observed phenomena. As a matter of fact, at the higher doses aliphatic amines are observed (see Table 3). The amines are formed in the acidified solutions, as well. Aromatic amines are not observed. The RNH_2 type amines in the irradiated solution of $[WH_4(dppe)_2]$ saturated with N_2+H_2 were found in the IR spectrum—ν(NH) at 3500 cm^{-1} and δ(NH) at 1640 cm^{-1}.

The other support for the presence of amines is its ^1H NMR spectrum, i.e. the signals at 0.8–1.8 ppm region, in fact, partially overlapped by the signals of dppe. Thus, $[W(N_2)_2(dppe)_2]$ is believed to be reduced by the W—H groups or the radicals R:



(4)

More detailed mechanism of the process was presented earlier.[1-5]

The complexes of $[XW(N_2R)(dppe)_2]$ (R = C_6H_{11} or ) were described in the literature.[20] Our work concerning the formation of diazenide complex and its transformation to amines is in progress. Actually, the probability of reactions 4a and 4b seems to be dependent on the concentration of W—H groups and the lower concentration of the groups the more likely reaction 4b. The yields of the radicals C_6H_{11} and C_4H_7O are lower than 6 ($G_R < 6$) in cyclohexane–thf mixture.[8] If the radicals were formed as a result of the radiation decomposition of the solvents the G_R value should have been higher than 120. Therefore, the radicals are assumed to be formed in the other way without the influence of radiation. This problem will be explained in the next paper. On the other hand, H_3N seems to be the main product of reduction, although the yields of amines are remarkable. Taking into account the entire yields of reduction, i.e. H_3N and RNH_2, the high catalytic ability of the $[WH_4(dppe)_2]$—thf—C_6H_{12}—N_2—H_2 system seems to be obvious.

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