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HYDRIDE COMPLEXES OF TUNGSTEN IN PHOTOCATALYTIC DINITROGEN REDUCTION

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Abstract—[$WH_4(dpmp)_4$] and [$WH_4(trifos)(PPh_3)$] complexes were used photochemically to reduce fixed molecular nitrogen. Tetrahydrofuran–cyclohexane (1 : 1) acidified and non-acidified solutions under UV irradiation were examined.

Nitrogen is one of the most inert molecules. Under atmospheric pressure and at room temperature it reacts only with lithium. Dinitrogen activation by fixing in metal complexes gives very low yields of reduction products.[1] During the search for a catalyst, which would allow efficient reduction of N_2 under normal conditions, it has been assumed that the application of additional factors (e.g. γ radiation) leads to significantly higher yields[2] and even C—N bond formation.[3] Discovery and application of a chemical equivalent of 'nitrogenasis' would make it possible to simplify the soil fertilization processes considerably.

Our research concerns replacing γ rays by UV radiation. Earlier reports about photocatalytic reduction of fixed nitrogen are relatively scarce. In 1977, Schrauzer and Guth[4] reported the N_2 photoreduction to ammonia using TiO_2. In 1978, Thomas *et al.*[5] investigated the process of C—N bond formation under flash photolysis conditions using [$M(N_2)_2(dppe)_2$] complexes (where M = Mo, W, dppe = $Ph_2PCH_2CH_2PPh_2$) with alkyl halides. In 1979, Pivovarov *et al.*[6] ascertained formation of small amounts of hydrazine under the irradiation of the acidified complex solutions by visible light. They used [MH_4L_4] complexes (where M = Mo, W and L = asymmetric monodentate phosphine) in ethanol. In 1991, Tennakone *et al.*[7] reported catalytic reduction of molecular nitrogen on hydrated iron(III) oxide with visible light.

In our previous paper, we reported the usefulness of the complex [$WH_4(dppe)_2$] in the photochemical reduction of molecular nitrogen.[8] Complexes of tungsten with phosphines show interesting spectral properties, e.g. [$W(N_2)_2(dppe)_2$] has one band in the visible range at 440 nm and two bands in the UV range at 370 nm.[9] The object of this work has been to examine the photocatalytic activity of [$WH_4(trifos)(PPh_3)$] and [$WH_4(dpmp)_4$] complexes [trifos = $Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2$, di-{bis-1,2-(diphenylphosphine)ethane}phenylphosphine; dpmp = Ph_2PCH_3]. As the strength of the tungsten–ligand bond increases with the increase of the ligand coordination so does thermodynamic stability; the trifos complex should give a higher yield than the previously examined dppe compound, and the dpmp complex should give the lowest yield. Obtaining increasing photochemical yields with increase of phosphine ligand coordination would also confirm that during dinitrogen reduction the central atom/ion electrons do not play a significant part. If the phosphine ligands are more strongly bonded to the central atom/ion, its electrons are shifted towards the phosphorus atom, so the yields of the processes employing these electrons should be lower.

EXPERIMENTAL

Methyldiphenylphosphine was synthesized from triphenylphosphine by the standard method.[10] Trifos was obtained from dppe ($Ph_2PCH_2CH_2PPh_2$)

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in the reaction of $Ph_2PCH_2CH_2PPh^-$ anion with 2-chloroethyldiphenylphosphine.[11] The above complexes were obtained from tungsten hexachloride in several steps: $[WH_4(trifos)(PPh_3)]$ through the stages of $[WCl_4(PPh_3)_2] \cdot CH_2Cl_2$[12] and $[WCl_4(trifos)]$[13] complexes and $[WH_4(dpmp)_4]$ according to ref. 14. $[WH_5(dpmp)_4]HSO_4$ and $[WH_5(trifos)(PPh_3)]HSO_4$ were prepared as previously.[15,16]

Samples of 10 cm³ with complex concentrations of 1×10^{-3}, 5×10^{-3} and 1×10^{-2} mol dm⁻³, saturated with a mixture of deoxygenated nitrogen and hydrogen (1:3), were irradiated in a cylindrical quartz vessel (diameter 2.5 cm). A tetrahydrofuran–cyclohexane (1:1) mixture (THF–cH) was use as solvent; the cyclohexane was added in order to minimize C_4H_8O insertion into the tungsten coordination sphere. The gases were bubbled through the vessel at 15 cm³ min⁻¹ (N_2) and 45 cm³ min⁻¹ (H_2), which ensured vigorous stiring of the solution. A 30 W Cole–Parmer 365 nm UV lamp was used to eliminate H_2 and to convert the hydride complexes into the unsaturated intermediate compounds $[W(trifos)(PPh_3)]$ or $[W(dpmp)_4]$[17]. In order to maintain constant concentrations, the gases were passed through washers and after their saturation by the solvent, they were introduced into the irradiated solutions of tungsten complexes. Two series of measurements for each complex's concentration were carried out: in acidified and non-acidified solutions. The concentration of sulphuric acid in the sample was 0.01 M (0.1 M in the case of the highest concentration of the trifos complex). In each of the above cases the irradiation periods were in the range 1–60 min. With times shorter than 4 min no measurable amounts of molecular nitrogen reduction products were formed. The reduced nitrogen reaction products were absorbed from the waste gases in a washer with an aqueous solution of sulphuric acid ($c = 1 \times 10^{-1}$ mol dm⁻³).

The light intensity of the lamp was determined using a ferrioxalate actinometer[18] and converted to THF–cH solution $E_{THF-cH} = 7.83 \times 10^{16}$ eV cm⁻³ s⁻¹). Hydrazine and ammonia were determined by spectrophotometrical methods as reported previously[2,3,8,9,15]. The concentrations of dinitrogen reduction products were measured both in the irradiated solution and in the washer with sulphuric acid.

RESULTS AND DISCUSSION

Plots of ammonia (Fig. 1) and hydrazine (Fig. 2) formation were made. They show the dependencies of product molecule numbers vs irradiation dose (the functions' courses are obtained by computer optimization). These figures present the sum-
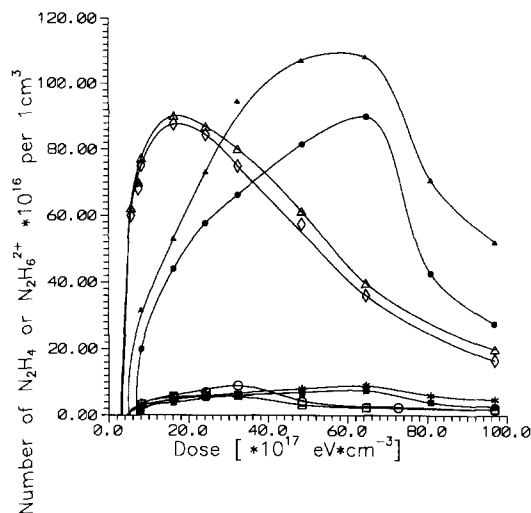

Fig. 1. Formation of hydrazine *vs* irradiation dose in UV-irradiated solutions. Solvent: THF–cyclohexane (1:1). $[WH_4(dpmp)_4]$ complex: $\bigcirc$, $c_{comp} = 1 \times 10^{-3}$ mol dm⁻³, $c_{acid} = 0$; $\square$, $c_{comp} = 1 \times 10^{-3}$ mol dm⁻³, $c_{acid} = 1 \times 10^{-2}$ mol dm⁻³; $\triangle$, $c_{comp} = 1 \times 10^{-2}$ mol dm⁻³, $c_{acid} = 0$; $\diamondsuit$, $c_{comp} = 1 \times 10^{-2}$ mol dm⁻³, $c_{acid} = 1 \times 10^{-2}$ mol dm⁻³. $[WH_4(trifos)(PPh_3)]$ complex: $*$, $c_{comp} = 1 \times 10^{-3}$ mol dm⁻³, $c_{acid} = 0$; $\blacksquare$, $c_{comp} = 1 \times 10^{-3}$ mol dm⁻³, $c_{acid} = 1 \times 10^{-2}$ mol dm⁻³; $\blacktriangle$, $c_{comp} = 1 \times 10^{-2}$ mol dm⁻³, $c_{acid} = 0$; $\bullet$, $c_{comp} = 1 \times 10^{-2}$ mol dm⁻³, $c_{acid} = 1 \times 10^{-1}$ mol dm⁻³.
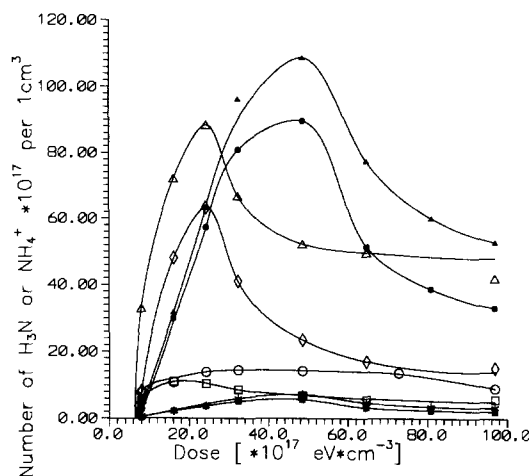

Fig. 2. Formation of ammonia *vs* irradiation dose in UV-irradiated solutions. Solvent: THF–cyclohexane (1:1). $[WH_4(dpmp)_4]$ complex: $\bigcirc$, $c_{comp} = 1 \times 10^{-3}$ mol dm⁻³, $c_{acid} = 0$; $\square$, $c_{comp} = 1 \times 10^{-3}$ mol dm⁻³, $c_{acid} = 1 \times 10^{-2}$ mol dm⁻³; $\triangle$, $c_{comp} = 1 \times 10^{-2}$ mol dm⁻³, $c_{acid} = 0$; $\diamondsuit$, $c_{comp} = 1 \times 10^{-2}$ mol dm⁻³, $c_{acid} = 1 \times 10^{-2}$ mol dm⁻³. $[WH_4(trifos)(PPh_3)]$ complex: $*$, $c_{comp} = 1 \times 10^{-3}$ mol dm⁻³, $c_{acid} = 0$; $\blacksquare$, $c_{comp} = 1 \times 10^{-3}$ mol dm⁻³, $c_{acid} = 1 \times 10^{-2}$ mol dm⁻³; $\blacktriangle$, $c_{comp} = 1 \times 10^{-2}$ mol dm⁻³, $c_{acid} = 0$; $\bullet$, $c_{comp} = 1 \times 10^{-2}$ mol dm⁻³, $c_{acid} = 1 \times 10^{-1}$ mol dm⁻³.

marized values of the product's molecule numbers (measured both in irradiated solution and in the washer).

Photochemical yields of dinitrogen reduction products are summarized in Table 1. Table 2 presents a comparison of catalytic efficiencies of the γ- and UV-irradiated systems.

The presented curves are similar for various complexes. For both hydrazine and ammonia an induction period and maximum occur (the ammonia curve for γ irradiation shows a distinct plateau). The presence of the induction period is connected to the low concentration of bis-dinitrogen complexes under short times of irradiation. As has been explained in previous papers, the lowering of hydrazine yields with increased radiation dose results from further N_2H_4 reduction to ammonia.[2,3,15,19-21] Maxima of H_3N formation curves, i.e. the lowering of ammonia yields at higher doses, arise from H_3N decomposition (the decomposition rate under UV
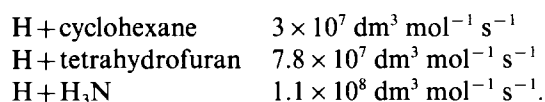
irradiation is higher than ammonia formation rate; under γ irradiation this relation is inverted).

This decay takes place in UV-irradiated systems in consequence of the reaction with R radicals:

$$L\text{—}M\text{—}H + S \xrightarrow{h\nu} M\text{—}L + H_2 + R$$
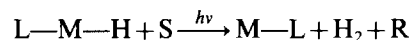
(S, solvent molecule; R, radical formed from S).

The rate constant increases in the following series of reactions:[22,23]

H + cyclohexane	3×10^7 dm^3 mol^{-1} s^{-1}
H + tetrahydrofuran	7.8×10^7 dm^3 mol^{-1} s^{-1}
H + H_3N	1.1×10^8 dm^3 mol^{-1} s^{-1}.

Considering solvent concentrations with molar ratio $1:1$, $c_{cH} = 6.15$ mol dm^{-3} and $c_{THF} = 4.63$ mol dm^{-3}, and the maximum H_3N concentration in acidified solution $c_{H_3N} = 1.5 \times 10^{-2}$ mol dm^{-3}. The probability of the H + THF reaction is 27 times

Table 1. Quantum yields of hydrazine and ammonia converted per 100 eV (measured both in the irradiated sample and in the washer)

Complex	Complex concentration (mol dm^{-3})	NH$_3$ yields		N$_2$H$_4$ yields	
		$c_{acid} = 0$	$c_{acid} = 0.01$ M	$c_{acid} = 0$	$c_{acid} = 0.01$ M
[WH$_4$(dpmp)$_4$]	1×10^{-3}	22.90	11.30	1.74	0.92
	5×10^{-3}	31.01	26.09	2.60	1.34
	1×10^{-2}	296.2	29.33	13.86	13.48
[WH$_4$(trifos)(PPh$_3$)]	1×10^{-3}	25.6	21.7	4.75	3.80
	5×10^{-3}	123.7	122.8	7.27	7.40
	1×10^{-2}	420.3	355.1[a]	26.64	25.67[a]

[a] Concentration of sulphuric acid was 0.1 mol dm^{-3}.

Table 2. Comparison of catalytic efficiencies in UV- and γ-irradiated systems for complex concentration of 0.01 M

	Number of cycles after absorption of 5×10^{18} eV (number of NH$_3$ moles per mole of W^{IV} complex)			
	γ		UV	
Complex	$c_{acid} = 0$	$c_{acid} = 0.01$ M[a]	$c_{acid} = 0$	$c_{acid} = 0.01$ M[a]
[WH$_4$(dpmp)$_4$]	1.42[b]	2.24[b]	2.60	1.00
[WH$_4$(dppe)$_2$]	8.10[c]	15.70[c]	3.90[d]	1.20[d]
[WH$_4$(trifos)(PPh$_3$)]	25.00[e]	41.00[e]	5.00	4.00

[a] $c_{acid} = 0.1$ M in the case of the trifos complex.
[b] According to ref. 24.
[c] According to ref. 2.
[d] According to ref. 8.
[e] According to ref. 26.

greater and the probability of the H+cH reaction is ~10 times greater than the probability of the H+H₃N reaction. With regard to the above, ammonia molecules react primarily with the radicals forming from THF, with C_6H_{11} in smaller part, and the reaction H+H₃N is of little importance.

Figure 3 presents an example of the distribution of global ammonia concentration between the irradiated sample and the acidic washer absorbing waste gases.

As shown in Fig. 3, the number of H₃N molecules in the washer shows a plateau for a range of UV irradiation doses. On the other hand, ammonia concentration in the UV-irradiated sample reaches a maximum and then decreases, and this can be explained by the secondary reactions. The plots in Fig. 3, are also in good accordance with the fact that the acid influence in the UV-irradiated field is the reverse of the one in the case of γ radiation, i.e. the presence of acid in the UV-irradiated samples leads to a decreased yield (see also Table 1). In the case of acidified samples, a smaller part of H₃N leaves the irradiated sample and is absorbed in the washer, and that is why the greater part of ammonia undergoes the reactions with radicals.

Figures 1 and 2 show the shift of the plots' maxima for various phosphine ligands. In the case of the dpmp complex, the irradiated systems reach maxima for doses lower than in the case of the trifos complex. The cause is the difference in thermodynamic stability
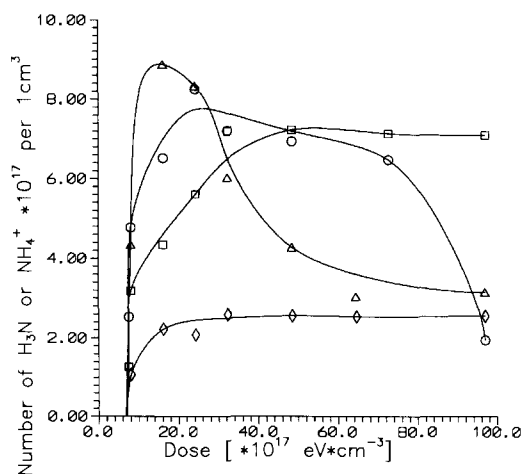
of the complexes: the trifos complex is more stable than the monophosphine complex ($E_{W-LLL} > E_{W-L}$). The hydride ions are liberated more readily from the dpmp complex so dinitrogen complex forms earlier, thus explaining the difference of N_2H_4 maxima. The subsequent reduction stages also require H⁻ ions,[15] which are bonded more strongly with tungsten in the trifos complex, and that is why H₃N maxima are also shifted.

Based on the above results and compared with the results obtained under irradiation, it can be assumed that the mechanism of the photolytic dinitrogen fixation and reduction using hydride complexes is similar to the mechanism of the radiation-catalytic process in analogous systems.[2,3,15,19-21,24]

UV radiation causes the elimination of hydrogen from the central atom coordination sphere and its replacement by N₂ addition, similarly as in γ-irradiation. Later, the reduction of molecular nitrogen and the formation of H_4N_2 and H₃N occur. In the range of lower doses (similarly as in γ irradiation) hydrazine complexes can decompose with hydrazine evolution. With increasing dose, the process of further hydrazine reduction to ammonia starts to prevail. In acid solution the complex $[WH(N_2)_2(dppe)_2]^+$ forms, which is known even in the solid state.[25]

UV irradiation, apart from the above-mentioned hydride ion elimination from the inner coordination sphere, also causes the dissociation of the bis-dinitrogen complexes, which are formed in nitrogen-saturated solution. The electron excitation in the UV-irradiated field weakens the tungsten–nitrogen π bond.

The lower yields of molecular nitrogen reduction to hydrazine and ammonia in the case of UV irradiation can also be explained by a lower reproducibility of the dinitrogen complex under UV irradiation. During γ irradiation the presence of reducing agents (e_s^-, R, H) stabilizes the W—N₂ bond. In UV-irradiated solutions, the concentration of the reducing agents is much lower (e.g. there are no solvated electrons). The attachment of an H⁺ ion to the central metal (in acidified systems) also destabilizes the M—N₂ bond. Thus, before the reduction can occur, the larger part of the complex decomposes and the number of cycles per molecule of catalyst is lower. The anticipated increase in photochemical yields with the increase in ligand correlation (see Table 2) is connected with the increasing bond stability in the series W—L < W—LL < W—LLL. The increasing thermodynamic stability in the above series stabilizes dinitrogen and phosphine ligands in the coordination sphere, and makes possible the increase in number of cycles of N₂ fixation and reduction.

Fig. 3. An example of ammonia distribution between the irradiated sample and the washer absorbing waste gases. System: [WH₄(dpmp)₄], $c_{complex} = 1 \times 10^{-3}$ mol dm⁻³; $c_{acid} = 0$ or 1×10^{-2} mol dm⁻³ (in irradiated solution); $c_{acid} = 1 \times 10^{-2}$ mol dm⁻³ (in the washer); solvent: THF–cyclohexane (1:1). ○, in irradiated neutral solution; □, in acidic washer, solution non-acidified; △, in irradiated acidic solution; ◇, in acidic washer, solution acidified.

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