Flash Photolysis of a Tungsten–Dinitrogen Complex. An Intermediate in the Formation of Carbon–Nitrogen Bonds

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Reactions of coordinated dinitrogen to form nitrogen–carbon bonds have been observed for a number of complexes of the type $[M(N_2)_2(dppe)_2]$ (M = W, Mo, Re; dppe = 1,2-bis(diphenylphosphino)-ethane) [1]. The reactions take place with acyl halides (M = Re, Mo, W) or alkyl halides (M = Mo, W) and the reactions with the alkyl halides are catalyzed by visible light. The products are complexes of the type $[MX(N_2R)(dppe)_2]$ and $[MX(N_2HR)(dppe)_2]X$. The reactions have been assumed to involve a free radical mechanism [2] in which alkyl radicals are generated from the alkyl halide or from the solvent (a butanol chain is incorporated in the product when the solvent is tetrahydrofuran, thf) [3]. No dinitrogen is evolved in the absence of alkyl halides.

Photochemical reactions of this type may have considerable potential in the photochemical fixation of nitrogen and the present flash photolysis studies have been undertaken in order to define the mechanism of carbon–nitrogen bond formation more precisely. The reactions proceed through a photochemically generated intermediate from which both coordinated dinitrogen molecules have been lost.

Experimental

The $[W(N_2)_2(dppe)_2]$ complex was prepared by the method of Chatt, Heath and Richards [4] and characterised by an $\epsilon = 2.7 \times 10^4\ M^{-1}\ cm^{-1}$ at 297 nm in thf. All operations with the complex and solutions were carried out in dry atmospheres and where necessary in completely sealed systems. Solvents were dried and distilled under N_2. Flash photolysis experiments were carried out using the standard techniques of this laboratory [5, 6] with the addition of an irradiation cell which allowed the solutions to be changed under controlled atmospheres.

Photolysis experiments with steady illumination were carried out with a tungsten (200 W) or a tungsten halogen lamp (100 W) as the light source, using interference filters to select the irradiation wavelength. In flash photolysis experiments identical results were obtained with or without a Perspex filter which eliminates wavelengths shorter than 300 nm. The concentration of the complex was determined by the intensity of the N–N infra-red stretch or by the absorbance at 297 nm in lower concentration solutions.

Results

Steady illumination of *ca.* $10^{-2}\ M$ solutions of the $[W(N_2)_2(dppe)_2]$ complex in dry thf saturated with nitrogen resulted in very little change (Table I). When the irradiation took place with the solution evacuated, or under argon, coordinated dinitrogen was lost rapidly. Irradiation of similar solutions saturated with CO or H_2 resulted in the production of the carbonyl, $[W(CO)_2(dppe)_2]$ and hydride, $[WH_4(dppe)_2]$ complexes respectively. In the presence of CH_3COCl or t-butyl bromide the organic group was incorporated at comparable rates. Previously [1] the reaction with CH_3COCl has been reported to require several hours at ambient conditions. The quantum yields for the reactions in Table I are somewhat uncertain but all lie between 0.3 and 0.7.

When the atmosphere above the thf solution of the complex was saturated with ^{15}N labelled dinitrogen ($^{15}N_2$ 48%; $^{14}N_2$ 46%; $^{14}N^{15}N$ 6%) irradiation resulted in the incorporation of the $^{15}N_2$ in the complex. The $^{15}N_2$ labelling experiments gave products with solution infra-red spectra which showed dinitrogen stretch peaks at 1948, 1904, and 1885 cm^{-1}, which can be assigned to the isotopomers $W(dppe)_2(^{14}N_2)_2$, $W(dppe)_2(^{14}N_2)(^{15}N_2)$ and $W(dppe)_2(^{15}N_2)_2$ [7]. On prolonged irradiation the ratio of the three peaks was 2.0:1:1. No incorporation of the $^{15}N_2$ occurred in the dark, and the $^{15}N_2$ complex did not lose the label when kept under an atmosphere of $^{14}N_2$ in the dark. It is apparent that the dinitrogen exchange occurs by the same type of dynamic light-induced process which is responsible for the photo-reactions with CO and H_2.

Flash photolysis experiments showed that an intermediate is formed following photo-excitation of $[W(N_2)_2(dppe)_2]$. When solutions of the complex ($4 \times 10^{-5}\ M$) in thf or benzene were flashed under dinitrogen or argon an immediate bleaching was observed. Solutions saturated with argon showed no further change. When the solutions contained dinitrogen, the bleached absorbance recovered to within 5% of the original value by a two-stage process. The change in transmittance with time at 297 nm is shown in Figure 1. The two stages of the recovery of the absorbance in N_2 saturated solutions were well separated in time (Figure 1) and the difference spectra at the end of the first recovery process, and

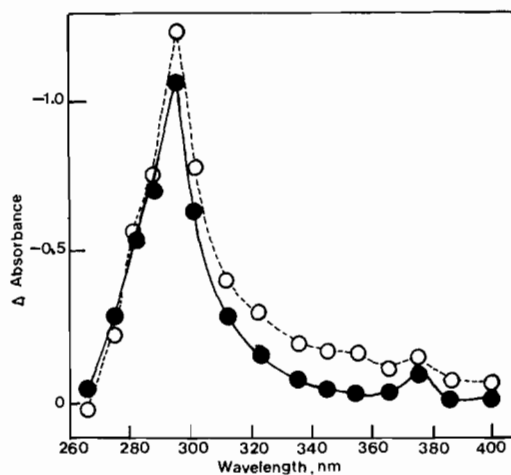TABLE 1. Steady Illumination Photolysis Experiments, Visible Light.

Conditions	$[W(N_2)_2(dppe)_2]$, M^a	Results
N_2 saturated	5×10^{-3}	*ca.* 5% decomposition, 6 hr
Ar saturated	2.5×10^{-3}	50% decomposition in 2 hr
Vacuum	2.5×10^{-3}	50% decomposition in 2 hr
CO saturated	2.5×10^{-3}	50% conversion to $[W(CO)_2(dppe)_2]$ in 45 min
H_2 saturated	1.6×10^{-3}	50% conversion to $[W(H_2)(dppe)_2]$ in 35 min
t-BuBr 0.05 M	2.9×10^{-3}	50% formation of $[WBr(N_2t-Bu)(dppe)_2$ in 50 min
CH_3COCl 0.05 M^b	2.5×10^{-3}	50% formation of $[WCl(NNCOCH_3)(dppe)_2]$ in 45 min
$^{15}N_2$ saturated	$5 \times 10^{-3\,c}$	50% labelled $[W(N_2)_2(dppe)_2]$ in 2 hr

^{a}Reaction volume 150 ml thf. ^{b}Negligible reaction in dark over comparable time period. ^{c}Reaction volume 5 ml.
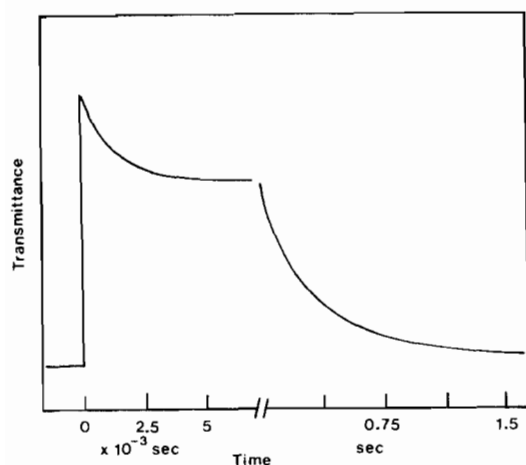
Figure 1. Changes in transmittance at 297 nm following flash photolysis of $[W(N_2)_2(dppe)_2]$, 4×10^{-5} M in thf saturated with N_2. Note change of scale on x-axis.

Figure 2. Difference spectra taken after flash photolysis of $[W(N_2)_2(dppe)_2]$ in thf saturated with N_2. $\bigcirc$, immediately following the flash; $\times$, 11.25 msec after the flash at the end of the first stage of the reactions shown in Fig. 1.

immediately after flashing are shown in Figure 2. By the conclusion of the second reaction almost all of the absorbance lost in the bleaching reaction was restored. The rate constants for the two processes of Figure 1 were first order, with rate constants of 3.9 ± 0.8 $\times 10^2$ sec^{-1} and 1.6 ± 0.3 sec^{-1} in thf saturated with N_2 at 25 °C. The quantum yield for the bleaching was the same for the solutions saturated with argon or dinitrogen, and the difference spectra taken immediately after the flash were the same.

When solutions saturated with CO were flashed, a bleaching, followed by a two stage recovery process was again observed, but the absorbance did not return to the original value, and at the completion of the reaction the product was the carbonyl complex $[W(CO)_2(dppe)_2]$. The rate constants for the formation of the carbonyl complex were very similar to those for the reaction of the bleached intermediate with dinitrogen and were 5.1 ± 0.4 $\times$ 10^2 sec^{-1} and 2.5 ± 0.4 sec^{-1}.

When N_2 saturated solutions of $[W(N_2)_2(dppe)_2]$ containing 2-bromobutane (0.04 M), which were prepared and handled in the dark, were flashed, the same

initial bleaching of the absorbance due to the dinitrogen complex was observed. The bleaching was followed by three identifiable reaction steps. An initial return towards the original absorbance was followed by a second, slower return which was competing with a third reaction which led to a permanent decrease in absorbance at 297 nm, where the final reaction product, $[WBr(N_2Bu)(dppe)_2]$ has a smaller absorbance than $[W(N_2)_2(dppe)_2]$. The initial reaction had the same rate constant as that for an N_2 saturated solution alone, 4.6 ± 0.8 $\times$ 10^2 sec^{-1}, and the second step was also similar to that in the absence of 2-bromobutane, with a rate constant of 3.9 ± 0.6 sec^{-1}. The third reaction which leads to a permanent change to form the product had a rate constant of 0.5 ± 0.1 sec^{-1}.

Similar results were obtained for solutions in benzene containing dinitrogen.

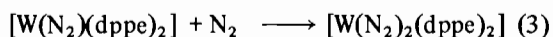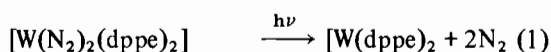Flash photolysis of solutions of $[W(N_2)_2(dppe)_2]$ in thf saturated with $^{15}N_2$ ($^{15}N_2$ 81%; $^{14}N^{15}N$ 10%; $^{14}N_2$ 9%) showed that dinitrogen exchange occurred after a single flash. The infra-red spectrum of the

solutions after one flash showed the nitrogen stretch absorbances at 1945, 1905, and 1885 cm^{-1}. It is significant that, although only a fraction of the coordinated dinitrogen is exchanged, both isotopomers $W(dppe)_2(^{15}N_2)_2$ and $W(dppe)_2(^{14}N_2)(^{15}N_2)$ are present in the solution.

Discussion

The steady illumination experiments show that light labilizes the dinitrogen in the complex, decomposition occurring when the photolyses were carried out under argon or vacuum. The labilized complex from which dinitrogen has been lost is able to take up CO, H_2. The dinitrogen-labelling experiments prove that the intermediate (or the photo-excited state) has been labilized for dinitrogen exchange. The role which has been assigned previously to the alkyl halide in assisting in the evolution of N_2 [1] is therefore clearly, at least in part, that of competing with the N_2 for the labilized metal centre.

The flash photolysis experiments provide clear evidence for the nature of the initial photochemical process. The loss of absorbance due to $[W(N_2)_2(dppe)_2]$ is coincidental with the flash and is not due to the formation of an excited state but to the loss of dinitrogen from the complex [8]. As the recovery of the original absorption under nitrogen is a two stage reaction we conclude that both the dinitrogen molecules must be lost in the first stages of the photo-reaction, although whether simultaneously or consecutively cannot be decided without experiments using laser excitation at shorter time resolution. In the presence of dinitrogen the reactions are

$$[W(N_2)_2(dppe)_2] \xrightarrow{h\nu} [W(dppe)_2 + 2N_2 \quad (1)$$

$$[W(dppe)_2] + N_2 \longrightarrow [W(N_2)(dppe)_2] \quad (2)$$

$$[W(N_2)(dppe)_2] + N_2 \longrightarrow [W(N_2)_2(dppe)_2] \quad (3)$$

The role of the solvent (thf or benzene) has not so far been defined. The rates of the first and second reactions are almost the same for N_2 and CO, suggesting that the reactions are governed by the rates of solvent exchange at the sites originally occupied by the two dinitrogen molecules. The $^{15}N_2$ exchange experiments in which exchange is induced by flash photolysis confirm that both dinitrogen molecules are lost from the complex upon photo-excitation.

The reactions in the presence of N_2 and 2-bromobutane indicate that it is the complex with only *one* coordinated N_2 which reacts with 2-bromobutane (and by implication, with other alkyl halides)

$$[W(N_2)(dppe)_2] + RX \rightarrow [WX(N_2R)(dppe)_2]$$
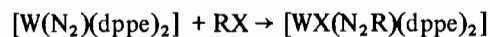
The competition between 2-bromobutane and N_2 shown in the flash experiments provides direct evidence for the proposed mechanism of formation of C–N bonds in these systems [2] in which homolytic fission of the R–X bond takes place at the metal centre [2] which has only one N_2 coordinated. The C–N bond may be formed either between the alkyl radical derived from the alkyl halide or one derived from the solvent by alkyl radical attack, and the one remaining coordinated dinitrogen. This first direct observation of a transient intermediate in the photochemical reactions of dinitrogen complexes indicates that it is the metal centre with only one coordinated N_2, and possibly of reduced coordination number, produced by photo-excitation and subsequent recombination with one N_2 molecule which is highly reactive towards carbon–halogen bonds. Systems of this kind have an obvious potential for the photochemical fixation of nitrogen using sunlight, and we are at present extending the work to other systems.

Acknowledgements

References

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6 A. T. Thornton and G. S. Laurence, *Int. J. Radiat. Phys. Chem.*, in press.
7 Assignments based on relative intensities of N–N absorptions of isotopomers under limiting conditions. Detailed arguments to be published elsewhere.
8 We have been unable to observe any long-lived emission which would indicate the presence of an excited state of the complex, and an excited state with a lifetime long enough to take part in the reactions with the rate constants we have measured (*ca.* 0.1 s or longer) is most unlikely in a stystem like $[W(N_2)_2(dppe)_2]$ which contains such a heavy atom as W.