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A FLASH PHOTOLYSIS STUDY OF THE ELIMINATION OF DINITROGEN FROM *trans*-$(N_2)_2W(dppe)_2$; dppe = 1,2-BIS-DIPHENYLPHOSPHINOETHANE

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Summary

Flash photolysis of *trans*-$(N_2)_2W(dppe)_2$ (1) at —60, —30, —10°C, and room temperature indicates that loss of dinitrogen occurs stepwise via the following proposed intermediates. Photodissociation of 1 gives the transient A decaying with $k_1 \sim 4450\ s^{-1}$ to the doubly coordinatively unsaturated species [W(dppe)$_2$], B. Further reactions of B are dependent on the type of gas used to saturate the solutions. In N_2-saturated media, B is efficiently reconverted into the starting complex 1 via $(N_2)W(dppe)_2]$, C(N_2), $k_2^{N_2} = 450\ s^{-1}$, which in turn takes up a second molecule of N_2, $k_3^{N_2} = 3.7\ s^{-1}$. In CO-saturated solutions, *trans*-$(CO)_2W(dppe)_2$ is produced as the final product and the corresponding rate constants are k_2^{CO} 1500 s^{-1} for B → C(CO) and $k_3^{CO} = 1.14\ s^{-1}$ for C(CO) → product. In Ar-saturated solvents, B is transformed, again in two steps; $k_2^{Ar} = 1\ s^{-1}$ and $k_3^{Ar} = 0.1\ s^{-1}$, to products of unknown structure.

The different rate constants $k_2^{N_2}$, k_2^{CO}, k_2^{Ar} and $k_3^{N_2}$, k_3^{CO} and k_3^{Ar}, together with the common activation energy of ca. 11 kcal/mol^{-1} for the three processes A → B, B → C(N_2) and C(N_2) → 1 suggest that the reactions of B and C occur by S_N2-type displacement of coordinated solvent molecules by the incoming ligands.

Introduction

There has been much recent work concerned with $(N_2)_2M(PR_3)_4$, M = Mo, W [1]. Most of the studies deal with methods of synthesis of such complexes, and with their reactions. The *trans*-$(N_2)_2M(dppe)_2$ (M = Mo, W) complexes are of special interest since they undergo novel photochemical reactions in addition to thermal reactions. Examples of the former are the reduction [2] and alkylation [3] of dinitrogen occuring upon irradiation of the tungsten complexes.

In connection with our investigations of the photochemical behaviour of transition metal complexes of diazenes and related nitrogen ligands [4,5], we have studied the emission properties of *trans*-$(N_2)_2W(dppe)_2$ (1) and of *trans*-$(CO)_2W(dppe)_2$ [6]. The relatively strong photoluminescence at 77 K ($\phi \sim 0.1$) disappears as the solvent 2-methyltetrahydrofuran becomes liquid at about 120 K, indicating effective deactivation of excited 1 [6]. To obtain information about these processes, we have performed flash photolysis experiments with 1 at various temperatures. A recent communication reported the room temperature flash photolysis investigation of light catalysed alkylation of 1 [7].

Results

Room temperature flash photolysis in Ar-, N_2- and CO-saturated solutions

Flash photolysis of an approximately 10^{-4} *M* argon-saturated solution of *trans*-$(N_2)_2W(dppe)_2$ (1) in benzene is followed by an increase in the absorbance of the solution at $\lambda > 480$ nm. Measurements at shorter wavelengths are hampered by the strong absorption of 1 (see Fig. 1). The transient produced has an absorption maximum at about 510 nm, measured 20 μs after the flash. The absorbance at 480—510 nm increased slightly up to ca. 400 μs after the flash while the absorbance at 530—550 nm decreased slightly during about the same period. The absorbance at 510 nm slowly decreases in an apparently two-step process and eventually stabilises at a value lower than that of the starting solution (Fig. 2a). Irreversible decomposition occurs to the extent of 50—60% per photolysis flash. Both decay processes obey first order kinetics and the rate constants, obtained by a computer regression line fit, are $k_2^{Ar} = 1.1 \pm 0.3\ s^{-1}$ (correlation coefficient $r = 0.990$) and $k_3^{Ar} = 0.13 \pm 0.03\ s^{-1}$ ($r = 0.994$) for the fast and slow reaction, respectively.

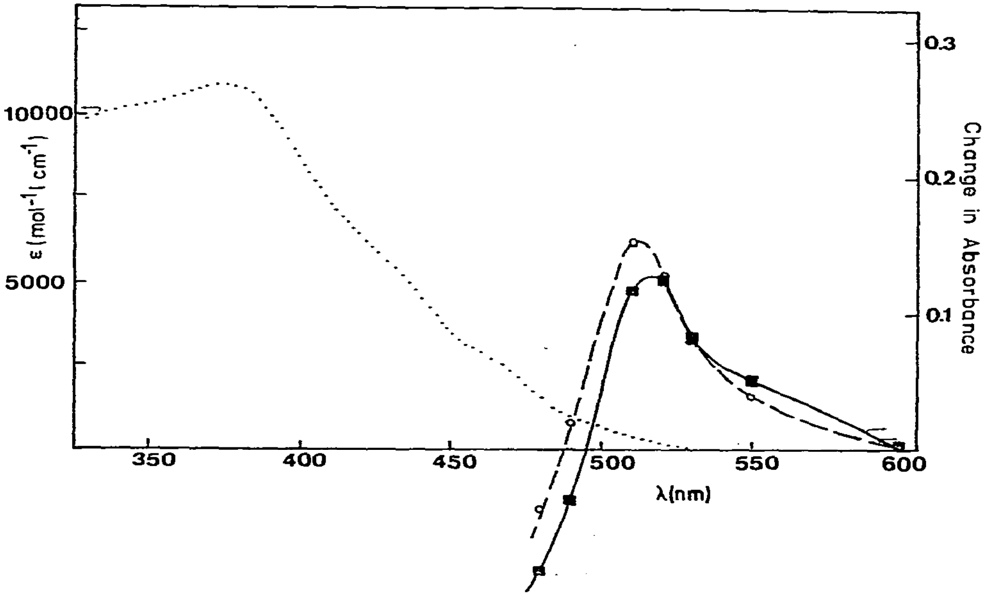

Fig. 1. Absorption spectrum of 1 (· · · · · ·) and difference spectra of intermediates formed by flash photolysis of 1 measured 20 μs (———) and 400 μs (- - - - -) after flash, in Ar-saturated benzene solution.

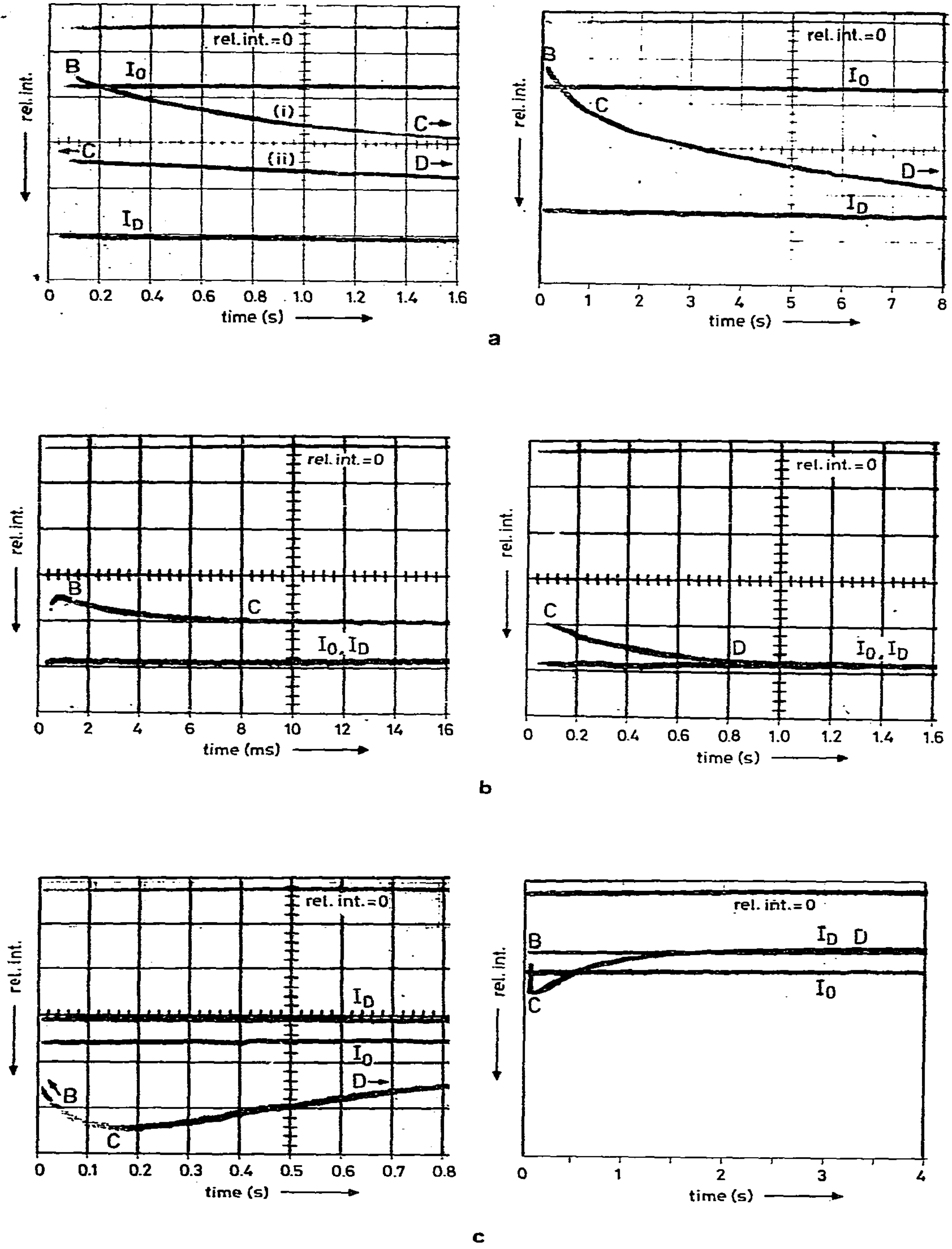

Fig. 2. Intensity of light transmitted at 510 nm by flashed benzene solutions of 1 as a function of time; (a) Ar-saturated (i) scan triggered by the flash (ii) scan triggered manually after scan (i), (b) N_2-saturated, (c) CO-saturated: I_0 = rel. int. before flashing, I_B = rel. int. at B, I_C = rel. int. at C and I_D = rel. int. at D, $t = \infty$ after flash.

Flash photolysis of dinitrogen-saturated benzene solutions of 1 also leads to an increase of absorbance at 510 nm. Again, a two-step decay with first order kinetics is observed. Between 20 μs and 100 μs after the flash, changes occur similar to those in argon-saturated solutions. The difference between the rate constants: $k_2^{N_2} = 450 \pm 50$ s^{-1} ($r = 0.997$) and $k_3^{N_2} = 3.7 \pm 1.1$ s^{-1} ($r = 0.994$) is larger than in the experiments under Ar. Fig. 2b shows an oscilloscope trace observed at 510 nm. The final intensity of the light transmitted (I_D) is only slightly higher than that before flashing, indicating almost complete regeneration of complex 1 *.

Flash photolysis of 1 in carbon monoxide saturated benzene solution does again lead to an initial increase of absorbance at 510 nm (Fig. 2c). The variation of absorbance with time again occurs in two steps, although the oscilloscope trace looks very different from those obtained in the experiments with Ar- and N_2-saturated solutions. This is because the final product, *trans*-$(CO)_2W(dppe)_2$, has a higher absorbance [8] than complex 1. Both the fast and slow reaction follow first order kinetics, and the rate constants are $k_2^{CO} = 1500 \pm 500$ s^{-1} ($r = 0.951$) and $k_3^{CO} = 1.14 \pm 0.31$ s^{-1} ($r = 0.971$).

Difference spectra were measured by flash spectroscopy at selected time intervals after the photolysis flash in the presence of the three gases described above. It was found that 30 μs and 300 μs after the flash, the same type of difference spectrum is obtained irrespective of the gas used to saturate the solution (Fig. 3a). This difference spectrum, with a maximum positive absorbance difference at approximately 510 nm and an apparent ** maximum negative difference at about 350 nm, is observed during the period of the fast reaction. At 3 ms after the flash, the general shape of the transient absorption has been mainly preserved, but for CO-saturated solutions, the transient absorbance at 510 nm is no longer greater than I_0, and the apparent absorbance minimum of both N_2- and CO-saturated solutions has shifted to ~390 nm. At 1s after the flash (Fig. 3c), solutions saturated with N_2 show essentially no effect, indicating that complex 1 has been reformed in the last reaction step. The Ar-saturated solution still exhibits a somewhat changed maximum negative absorbance difference but almost no positive one. The spectrum of the CO-saturated solution is nearly unchanged except that the absorbance difference at 510 nm is now positive. The identity of this last difference spectrum with the difference between the absorption spectra of the flashed and unflashed solution, measured conventionally, demonstrates the reliability of these measurements. The *trans*-$(CO)_2W(dppe)_2$ formed in the last reaction step has been identified by UV and IR spectroscopy (see Experimental Section).

Low-temperature flash experiments

Since preliminary laser flash experiments indicated that the absorbance of 1 is bleached instantly (< 20 ns) and that processes faster than those described above were also occurring, we carried out low-temperature conventional flash

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* It appears that decomposition is due to reaction with traces of air or impurities since it was often observed that flashing of fresh solutions caused more decomposition than flashing of already photolysed solutions, while repeatedly flashed solutions often did not decompose further.

** The sensitivity of the spectrographic setup used falls drastically at shorter wavelengths.

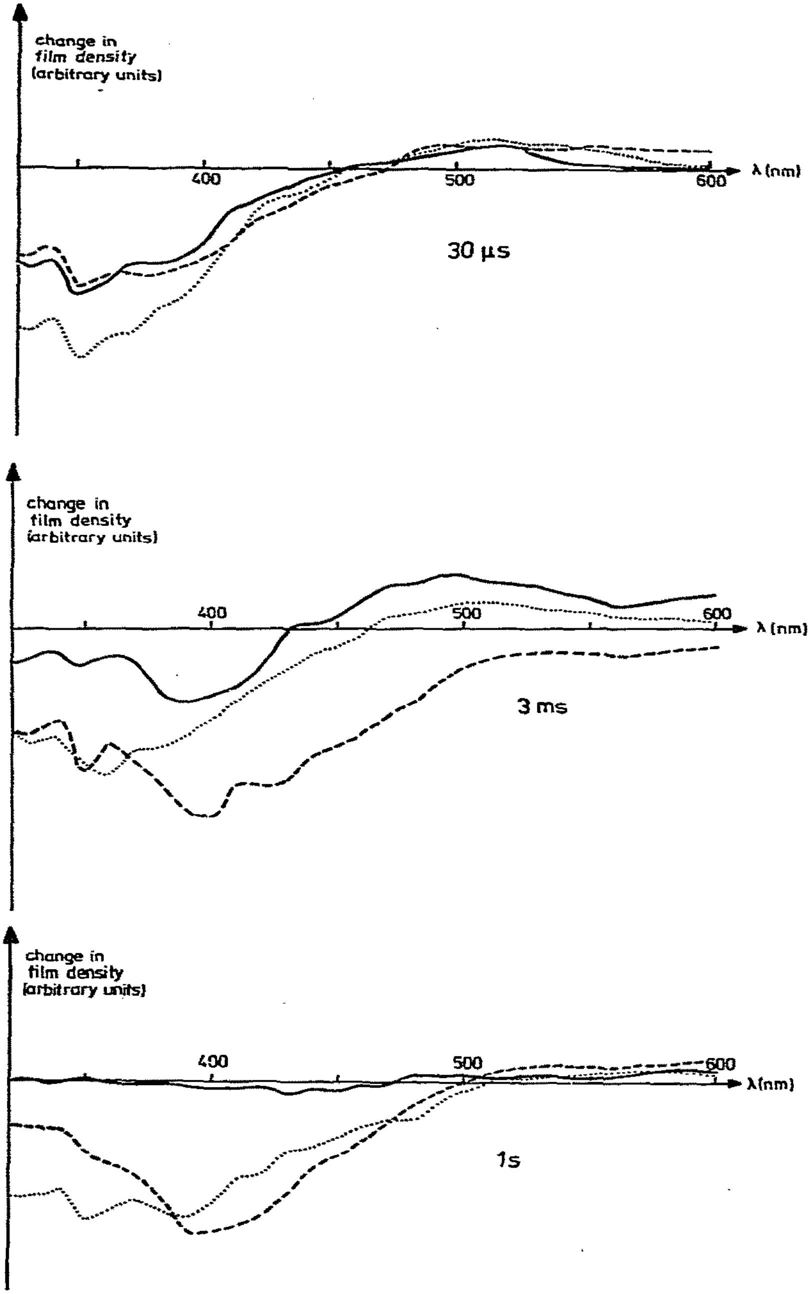

Fig. 3. Difference spectra of intermediates formed (a) 30 μs, (b) 3 ms and (c) 1s after flashing 1 in benzene solutions: ———, - - - - - -, · · · · · · correspond to N_2-, CO- and Ar-saturated solutions respectively.

photolysis of 1 in N_2-saturated toluene solutions. Fig. 4 shows a typical oscilloscope trace obtained at —30° C by monitoring the change of light intensity transmitted at 510 nm. Identical effects were obtained upon placing 3 mm Plexiglas filters (λ cutoff ~400 nm) between the flashtubes and the cuvettes. It

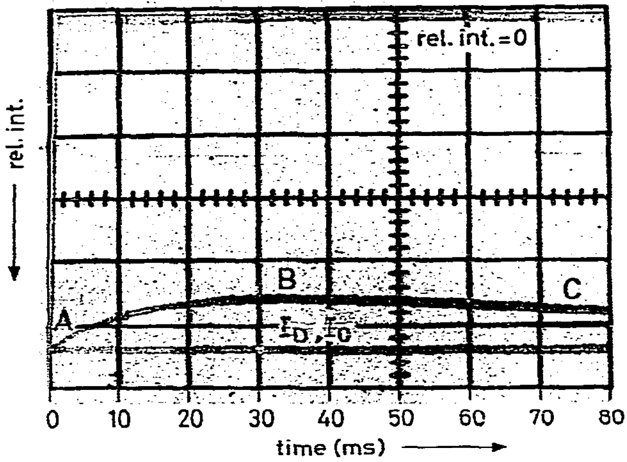

Fig. 4. Intensity of light transmitted at 510 nm by flashed toluene solutions of 1 as a function of time; —30°C.

is seen that, in contrast to the room temperature experiment (Fig. 2b), the initial increase of absorbance is slow enough to be easily followed. Activation energies were calculated for the grow-in process A → B (Fig. 4) and for the two decay processes B → C and C → D (Fig. 2b) with the help of approximate rate constants at various temperatures. Rate constants were obtained from the half life of the absorbance changes involved (Table 1).

TABLE 1

RATE CONSTANTS FOR THE PROCESSES A → B, B → C and C → D AT VARIOUS TEMPERATURES IN N_2-SATURATED TOLUENE SOLUTIONS

Process	T(°C)	$k = \ln 2/\tau_{1/2}$ (s^{-1})	$1/T \times 10^3$ (K^{-1})	ln k
A → B	—60	6.7	4.7	1.9
	—30	89	4.1	4.5
	—20	240	4.0	5.5
	—10	390	3.8	6.0
	0	14000	3.7	7.7
	ln A = 25		E_a = 10 kcal mol^{-1}	(r = 0.98)
B → C	—60	0.23	4.7	—1.5
	—30	6.4	4.1	1.9
	—20	14	4.0	2.6
	—10	43	3.8	3.8
	0	115	3.7	4.7
	20	280	3.4	5.6
	ln A = 25		E_a = 11 kcal mol^{-1}	(r = 0.99)
C → D	—10	0.38	3.8	—0.97
	0	0.87	3.7	—1.39
	20	3.9	3.4	1.36
	ln A = 24		E_a = 13 kcal mol^{-1}	(r = 0.86)

From these data, the rate constant for process A → B at room temperature is found to be approximately 4800 s^{-1}, while the extrapolated rate constant for B → C, 608 s^{-1}, matches that observed at room temperature (450 ± 50 s^{-1}). The process A → B is also observable in room temperature experiments in benzene solutions but the observable change in absorbance is too small to allow accurate measurement of the rate constant. The approximate lifetime of A, 0.1 ms, corresponds to that extrapolated from the Arrhenius plot (0.2 ms).

Discussion

The processes observed are summarized in Figure 5. The difference spectra measured by flash spectroscopy 30 μs and 300 μs after the flash are largely similar irrespective of the gas used to saturate the solution. The point by point spectra under argon and dinitrogen show, however, that slight changes occur between 20 μs and 400 μs after the flash (Fig. 1). From the fact that both a slight grow-in of absorbance at λ = 510 nm and a slight decay of absorbance at $\lambda > 530$ nm occur during this time, we consider it likely that an intermediate A is formed first from the excited state(s) of 1 and then decays to give a second transient B, the transient A having an absorption maximum to the red of that of B (510 nm). Further evidence for the existence of A is provided by the low temperature experiments, where it is seen that the grow-in of absorbance at 516 nm covers a span of ca. 1 s at −60° C. This is far too slow for a reaction from an excited state of 1, the longest-lived photoluminescing state detected having a lifetime τ = 19 μs at −196° C. The rate of the process A → B is also too slow for a solvation reaction which, by comparison with the reaction of $Cr(CO)_5$, with benzene [9], should have a rate constant of ca. 10^7 s^{-1}. Since the shapes of the difference spectra up to 300 μs are independent of the gas used to saturate the solution, A and B must be formed from 1 without the involvement of ligands in solution. From these observations we conclude that intermediate B is [W(dppe)$_2$]. The possibility that B has the composition [(N_2)W(dppe)$_2$] can be excluded on the basis of the observed two-step transformation of the absorbance of B to that of the final products. This is further supported by the various difference spectra 3 ms after flashing indicating that further reactions are dependent on the kind of gas used to saturate the solution. In the presence of N_2, B seems to be reconverted into 1 via intermediate C(N_2), while CO-saturated solutions give rise to the formation of *trans*-$(CO)_2$W(dppe)$_2$ via the intermediate C(CO) (Fig. 3). In the presence of Ar, B decays to products of unknown composition. From this evidence we propose that C(N_2) and C(CO) are [LW(dppe)$_2$], L = N_2 and CO, respectively, while the nature of C(Ar) is unknown at the present. A direct one-step conversion of B into the end products is very unlikely in view of the well documented consecutive elimination and addition of single ligands in the photochemistry of $L_xM(CO)_y$ complexes [10]. However, a possible concurrent formation of C by reaction of N_2 or CO with A cannot be excluded at present. The linear dependence of the concentration of the intermediates B and C(N_2) on the flash intensity indicate that only one photochemical step is involved in the formation of B and C from 1, and we propose the scheme depicted in Fig. 5 to rationalize the photochemical behaviour of complex 1.

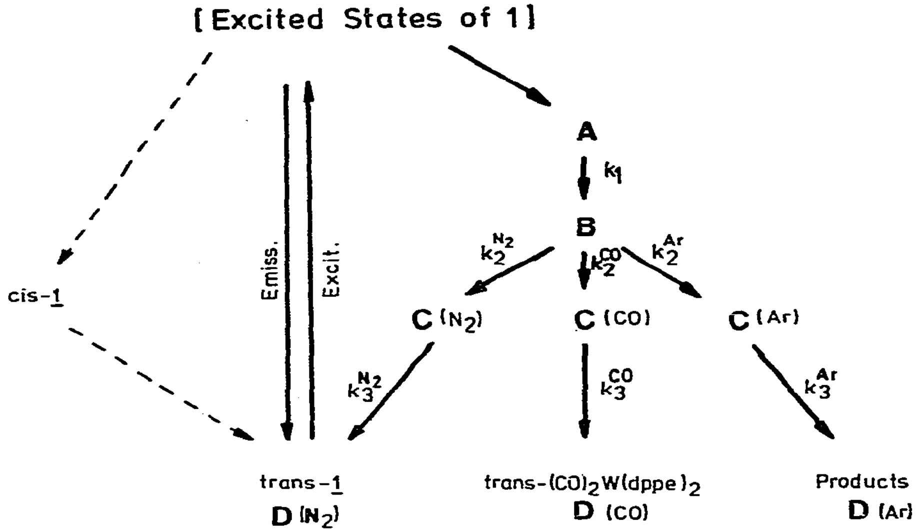

Fig. 5. Proposed scheme of photochemical behaviour of 1 in Ar-, N_2-, and CO-saturated benzene solutions; the intermediates probably contain coordinated solvent molecules.

Photochemical excitation of 1 results in the formation of at least two excited states as demonstrated by our emission studies at 77 K. Both emissions occur at 565 nm and have lifetimes of 50 ns and 19 μs [6,8]. Deactivation of 1^* at room temperature occurs predominantly via loss of N_2, although *trans*—*cis* isomerization might occur to a certain extent. This is suggested by steady illumination experiments in N_2-saturated toluene solution which result in the appearance of a weak IR band at $\bar{\nu} = 2018$ cm^{-1} assigned to one of the two $\nu(N{\equiv}N)$ modes of the *cis* isomer of 1. When the irradiation is stopped, this band disappears and the *trans* isomer is regenerated in a slow reaction (20 min).

The experiments indicate that the formation of B occurs via transient A. This reaction has an approximate rate constant k_1 of 4800 s^{-1} at room temperature as extrapolated from an Arrhenius plot. The nature of A is unknown but merits some speculation. It is unlikely to be an excited state of 1, since the conversion to B has an approximate activation energy of 10—11 kcal/mol and since two molecules of N_2 have to be eliminated in one single reaction step. We therefore assume that A is formed by loss of N_2 from 1^* and that it contains a strongly labilised W—N_2 bond, resulting in an efficient loss of this second N_2 molecule. If it is assumed that N_2-elimination occurs from a charge transfer to ligand excited state of 1 containing a partially oxidised tungsten center, it may be compared to the known lability of N_2 in the ground state of the oxidised complex *trans*-$[(N_2)_2Mo[I](dppe)_2]\ I_3$ [11].

The coordinatively doubly unsaturated intermediate B probably contains coordinated solvent molecules, by comparison with $Cr(CO)_5$ which takes up one molecule of benzene in a very fast reaction ($k = 7 \times 10^5$ l mol^{-1} s^{-1}) [11]. The rate of the reaction of B with CO, $k_2^{CO} = 1500$ s^{-1}, agrees well with that of analogous reaction of a diazaferrole in CO-saturated benzene solution: $(L)Fe(CO)_3 + CO = (L)Fe(CO)_4$, $k = 1500$ s^{-1}, measured in this laboratory [4]; the comparison of a doubly coordinatively unsaturated d^6-complex fragment with a d^8-species having only one vacant coordination site seems to be justified because the resulting d^6-singly unsaturated intermediate, C(CO), has a remarkable kinetic stability. An analogous complex, namely (CO)Mo(dppe)$_2$, is even stable enough to be isolated [12,13]. This agrees with the very low rate constant for the second recombination step, C(CO) → *trans*-(CO)$_2$W(dppe)$_2$, k = 1.14 s^{-1}. As proposed for species B, C might also contain a coordinated solvent molecule. The recombination rate of B with N_2, $k_2^{N_2}$ is 450 s^{-1} is much slower than that with CO. That can be explained in terms of FMO-considerations [14]; since the higher energy of the σ-HOMO of CO and its larger amplitude [15] at the coordinating carbon atom should result in a faster reaction rate. The same type of argument cannot be applied for explanation of the different rates of process C → D in N_2- and CO-saturated solutions without a detailed knowledge of the frontier molecular orbitals of C(CO) and C(N_2). The different rate constants observed in N_2- and CO-saturated solutions and the activation energies of 10—11 kcal/mol for processes B → C and C → products point to an S_N2 type substitution of coordinated solvent molecules by N_2 or CO.

The geometrical structures of the intermediates proposed cannot be assigned from the data available. By analogy to the square pyramidal geometry of (CO)-Mo(dppe)$_2$ [13], we assume the same structure for intermediates C(CO) and also for C(N_2), which has the same type of difference spectrum as C(CO) at the time 3 ms after the flash (Fig. 3b). Although an optimum C_{2v} geometry has been calculated for a d^6-M(CO)$_4$ fragment [16], we do not extrapolate this to the M(dppe)$_2$ moiety. The crucial point of the scheme is the structural difference between A and C(N_2) which are proposed to be isomers. Whereas A is formed from an electronically excited state, C(N_2) is generated in a ground state reaction. Depending on the detailed mechanism of the photodissociation of 1, A could therefore be formed in an electronically or vibrationally excited state. This might lead to a different, probably weaker W—N_2 bond compared to C(N_2). From the fact that 1 (*trans*) forms nearly exclusively *trans*-products, it seems unlikely that geometrical isomerization occurs in steps A to C. No literature data were available for metal fragments such as B, and both stereochemical rigidity [17] and full fluxionality have been proposed for pentacoordinated M(CO)$_5$ intermediates [18]. Low temperature photolysis of 1 with IR and UV monitoring is in progress to test the assumptions made on the structure of the intermediates.

One part of our work corroborates the results of Diamantis et al. [7] obtained independently at the same time. The reported rate constants, obtained from absorbance changes at λ = 297 nm, for process B → C, C → products, are 390 ± 80 s^{-1} and 1.6 ± 0.3 s^{-1} in N_2-saturated tetrahydrofuran, and 510 ± 40 s^{-1} and 2.5 ± 0.4 s^{-1} in CO-saturated tetrahydrofuran, respectively. The fact that the rate constant for process B → C(CO) in benzene solutions, as determined in our work, is much larger than in tetrahydrofuran, points to a better stabilisation of the coordinatively unsaturated intermediate B in the latter solvent. The other part of our work, detection of different excited states of 1, detection of A, a precursor of B, and measurement of activation energies for the different reaction steps, have solved some open questions and given a deeper insight into the nature of processes occuring upon photoexcitation of the dinitrogen complex.

Experimental

A sample of complex 1 was prepared according to the literature method [20]. Analysis gave the following values: Found: C, 60.06; H, 4.67; N, 5.36; P, 11.79; W, 17.62. $C_{52}H_{48}N_4P_4W$ calcd.: C, 60.24; H, 4.67; N, 5.40; P, 11.95; W, 17.74%.

Toluene and benzene were refluxed and distilled from sodium under argon before use. The purity was determined gas chromatographically to be 99%. Low temperature and room temperature flash photolysis were carried out using the standard methods of these laboratories [8,19]. Electrical (flash) energy in the room temperature experiments was 25 J for 5 cm cuvettes, 50 J for 13 cm cuvettes, flash duration was ca 3 μs but straylight duration was ca 10 μs. The low temperature apparatus used 10 cm cuvettes and electrical energy was 300 J; stray light was 500 μs at —30° C. All solutions were saturated with the test gas by bubbling the gas through the solution. The gas was bubbled through a wash bottle filled with solvent to prevent evaporation of the solution. The cuvettes were flushed with the test gas and filled using Schlenk-tube techniques. Solutions saturated with carbon monoxide and argon were handled under dim red safelights. Solutions used were 10^{-4} to 10^{-5} molar in complex 1.

The rate constants were determined by a computer program. This divides the I_0 and I_t values and takes the logarithm to give a set of readings (E). A synthetic base line can now be introduced to give E_{corr} values. The position of this base line above the real one can either be set at a fixed arbitrary value or optimized by calculation. The kinetic data is obtained from a linear regression analysis of plots of $1/E_{\mathrm{corr}}$ and $\ln E_{\mathrm{corr}}$ against time for the second and first order treatments, respectively.

In the presence of dinitrogen, repeated flashing caused no change in the shape of the electronic absorption spectrum of the solution, as measured on a Cary 17 recording spectrophotometer. The absorbance decreased slightly and uniformly upon photolysis. In the presence of carbon monoxide, the spectrum changed considerably after one flash and showed increased structure indicative of the presence of *trans*-$(CO)_2W(dppe)_2$ rather than *cis*-$(CO)_2W(dppe)_2$. To test this, constant irradiation experiments were carried out in a 0.05 mm IR liquid cell, filled with a carbon monoxide saturated tetrahydrofuran solution of complex 1, using a Philips HPK 125 W mercury lamp. An IR spectrum taken of the irradiated solution showed that the band at 1950 cm^{-1} due to $\nu(N_2)$ had disappeared almost completely and that a large band at 1814 cm^{-1} had appeared, as well as weaker bands at 1858 cm^{-1} and 1785 cm^{-1}. This showed that the major product formed is *trans*-$(CO)_2W(dppe)_2$, $\nu(CO) = 1813$ cm^{-1} in THF [8]. Some *cis* isomer, $\nu(CO) = 1851$ cm^{-1}, 1780 cm^{-1}, (CH_2Cl_2) [18] * is also formed, although this could be due to a thermal reaction, while it cannot be excluded that traces of $(CO)(N_2)W(dppe)_2$ $\nu(N_2) = 2128$ cm^{-1}, $\nu(CO) = 1799$ cm^{-1} (benzene) [13] are formed. Similar experiments were carried out by irradiating N_2-saturated toluene and tetrahydrofuran solutions of complex 1 in the IR liquid cell. The IR spectrum, taken immediately after the irradiation, shows that,

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* The compound *cis*-$[W(CO)_2(dppe)_2$ synthesised according to ref. 21a was found to have $\nu(CO)$ at 1855 and 1795 cm^{-1} in the infrared spectrum measured in tetrahydrofuran solution.

while the strong band at 1950 cm^{-1} becomes smaller, a very weak band at 2010 cm^{-1} shifts to 2018 cm^{-1} and becomes stronger and broader. The original spectrum is reestablished over 20 minutes upon standing of the cuvette in the dark.

It should be noted that, at low temperatures, an increase in absorbance is seen immediately after the flash decreasing with a rate about ten times as fast as process A → B. However, since this effect increases in magnitude upon repeated flashing, while all other effects decrease, it is probably due to a side reaction not involved in the generation of the intermediates observed.

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