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The Effect of the Wavelength of Light upon the Extent of Dinitrogen Exchange in Bis(dinitrogen) Complexes of Molybdenum and Tungsten [1]

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Of all the dinitrogen complexes of the transition metals that are presently known, the bis(dinitrogen) complexes of molybdenum and tungsten have shown the most diverse chemistry [3]. Nitrogen–hydrogen and nitrogen–carbon bonds have been formed using a variety of protic acids and of alkyl halides, respectively. In the original report of the reaction of methyl iodide with $Mo(N_2)_2(dppe)_2$ (*1*) (where dppe = 1,2-bis(diphenylphosphino)ethane) to form the methyldiazenido complex, $MoI(NNCH_3)(dppe)_2$ (equation 1) the effect of light upon the qualitative rate of reaction was noted [4].

$$Mo(N_2)_2(dppe)_2 + CH_3I \rightarrow MoI(NNCH_3)(dppe)_2 + N_2 \qquad (1)$$

While the reaction did occur in the dark, the rate of reaction as determined by rate of product formation was considerably faster in light [5]. In this Communication we wish to report our results of a study of the effect of the wavelength of light upon the extent of dinitrogen exchange (equation 2) for the following bis(dinitrogen) complexes of molybdenum and tungsten; *1*, $Mo(N_2)_2(depe)_2$, *2* (where depe = 1,2-bis(diethylphosphino)ethane) and $W(N_2)_2(dppe)_2$, *3*. It was hoped that these studies

$$M(^{14}N_2)_2(L_2)_2 + {}^{15}N_2 \rightarrow (M(^{14}N_2)(^{15}N_2)(L_2)_2 + {}^{14}N_2 \qquad (2)$$

$$[M = Mo,\ L_2 = dppe \text{ or } depe;\ M = W,\ L_2 = dppe]$$

would complement work already in progress in the elucidation of the electronic absorption spectra of the bis(dinitrogen) complexes of molybdenum and tungsten by other workers (*vide infra*).

Experimental

All solvents were reagent grade and were dried and distilled under dinitrogen immediately before use $Mo(N_2)_2(dppe)_2$ and $Mo(N_2)_2(depe)_2$ were prepared by a standard procedure [6]. $W(N_2)_2(dppe)_2$ was prepared by modification [7] of a published procedure [8].

Solutions for photolysis experiments were made up in a Vacuum Atmosphere Corp. Dri Box with a $^{14}N_2$ atmosphere. All solution preparations, degassing and thermostatting operations were performed in the dark or under a red photolab safelight. In all experiments a 20 mL aliquot of a 5.0×10^{-3} *M* solution of the $^{14}N_2$-labelled complex was placed in a 50 mL pyrex round-bottomed flask to which had been fused a 20 × 70 mm cylindrical quartz tube. By means of a vacuum stopcock the flask was attached to a vacuum line and the solution taken through three freeze–pump–thaw cycles. While still frozen at 77 K, 1.0×10^{-3} mol of $^{15}N_2$ gas [9] was introduced *via* the vacuum line. Upon warming to 300 K in a constant temperature bath, the flask was disconnected from the vacuum line and tilted so that the solution emptied into the cylindrical tube which was then mounted 1 cm from the exit slit of a 90° Farrand Optical Co., Inc., standard single grating monochromator. The entrance and exit slits, both 2 mm, were calculated from the manufacturer's reported dispersion of the grating to yield a 20 nm band pass. Irradiation was carried out using a Hanovia medium-pressure 550-W mercury lamp. Solutions were rapidly stirred during irradiation by means of a small magnetic stirring bar and maintained at 300 ± 0.1 K by means of a constant temperature circulating bath. Exchange experiments were performed in toluene and tetrahydrofuran (THF) solutions for each complex irradiating at 313 nm, 366 nm, 436 nm and 546 nm, and in the dark [10]. Quantum yields (see Table I) were determined using potassium ferrioxalate actinometry [11]. Light intensities were about 1.0×10^{-5} Einsteins/minute. In each experiment, the solution was irradiated for 1 hr after which time the vessel was rapidly transferred to the vacuum line and the solution cooled in liquid nitrogen. After the solution was frozen, a gas sample was removed for analysis of the $^{14}N_2/^{15}N_2$ ratio in the vapor phase using an AEI MS5076 mass spectrometer. Corrections were made for instrument background interference from air in the spectra by measuring the relative intensity of the m/e = 32(O_2) peak and subtracting the predetermined ratio of m/e 28:32 before working up the final data for the $^{14}N_2$ ratios obtained. We wish to thank Dr. Phil Lyon for his assistance.

Results

Photolysis of toluene solutions of *1*, *2* and *3* under $^{15}N_2$ gas for one hour produced a mixture of the

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TABLE I. Photodissociation Quantum Yields for Bis(dinitrogen) Complexes[a] and Electronic Absorption Spectral Data.[b]

Complex	Wavelength, nm[b]			λ, nm (ϵ_{max} M^{-1} cm^{-1})
	313	366	436	
$Mo(N_2)_2(dppe)_2$ (*1*)[b]	0.018	0.014	0.010	306(23,700), 377(13,700), 440(7500)sh
$Mo(N_2)_2(depe)_2$ (*2*)[c]	0.0040	0.0030	0.0036	327(38,600), 457(640),487(700)
$W(N_2)_2(dppe)_2$ (*3*)[c]	0.0037	0.0025	0.0027	297(27,200), 375(14,200), 440(6800)sh

[a] Calculated from the change in $^{14}N_2/^{15}N_2$ ratio at 300 K in the vapor phase; ±20%. [b] Toluene solution, room temperature. [c] Correction has been made for the thermal component of the exchange. [d] No exchange occurred in the dark at 300 K.

three isotopomers; *e.g.*, $M(^{14}N_2)_2(L_2)_2$, $M(^{14}N_2)(^{15}N_2)(L_2)_2$ and $M(^{15}N_2)_2(L_2)_2$. After each experiment, the products were analyzed by infrared spectroscopy. It was found that very little of the bis($^{15}N_2$) isotopomer was present and the initial isotopomer was the predominant species remaining. The extent of single exchange never exceeded 15% of that theoretically possible. The quantum yield data for the photodissociation of dinitrogen for the three complexes in toluene are given in Table I. It has been shown that whereas *1* exchanges N_2 in the dark at room temperature *3* does not [12].

We have found that *2* also does not exchange N_2 in the dark over a period of one hour. The quantum yield data for *1* have been corrected for thermal exchange. Compound *1* shows a very small increase in the extent of photodissociation as the wavelength of light decreases. However, compounds *2* and *3* (a) show no effect of change of wavelength of light upon the quantum yields within experimental error, (b) exhibit almost identical quantum yields and (c) exchange N_2 at a significantly slower rate than *1*.

Data were determined for irradiation at 546 nm but because of the unreliability of light intensities determined by ferrioxalate actinometry at this wavelength no quantum yields are reported. No exchange occurred for compounds *2* and *3* whereas *1* showed about the same amount of exchange at this wavelength. The quantum yield data for *2* and *3* in THF solution at all wavelengths studied were almost identical to the data obtained in toluene. However, the data gathered in THF solution for *1* was unreliable mainly due to nonreversible loss of N_2 ligands at these low N_2 partial pressures.

Discussion

It has been shown that the thermal $^{14}N_2/^{15}N_2$ exchange of *1* [12] and organonitrile substitution reactions of *1* [13], when carried out under pseudo first order conditions, obey first order kinetics with the loss of one dinitrogen ligand as the rate determining step. For our experiments to determine the effect of the wavelength of light upon the rate of dinitrogen exchange, we chose a sampling method for determining the quantity of exchange that had occurred in a given period of time. We deliberately conducted the experiments under non-pseudo first order conditions in order to minimize the amount of secondary exchange; *e.g.*, equation 3.

$$\underset{1a}{Mo(^{15}N_2)(^{14}N_2)(dppe)_2} + {}^{15}N_2 \rightarrow \underset{1b}{Mo(^{15}N_2)_2(dppe)_2} + {}^{14}N_2 \qquad (3)$$

Hence, each time one $^{14}N_2$ ligand dissociated from *1* there was a high probability that it would react with the five coordinate intermediate $[Mo(^{14}N_2)(dppe)_2]$ in competition with $^{15}N_2$. In this way very little *1b* would be formed, and therefore the exchange that we were looking at is represented by equation 2. The quantum yields determined [14] (see Table I) reflect the amount of exchange occurring under the conditions of these experiments. All experiments were conducted under identical conditions (except for small variations in the partial pressures of $^{15}N_2$). Therefore, these date cannot be compared either with the flash photolysis results reported by Diamantis *et al.* for the $W(N_2)_2(dppe)_2$ system [15] or our thermal data (identical conditions) compared with those already mentioned (*vide supra*) [12, 13]. However, our data are internally consistent and the quantum yields are relative values.

The prevailing theory, based upon spectroscopic and photochemical evidence, assigns the lowest excited states in low-spin d^6 complexes to the ligand field (LF) $^{1,3}E(e^3b_2^2a_1^1)$ states [16–18]. These states correspond to the $d_{z^2}(a_1)$ orbital which is σ^* with respect to the $M–N_2$ bond and population of which will labilize the $M–N_2$ bond [16, 19]. Correspondingly, depopulation of the d_{xz}, $d_{yz}(e)$ orbitals will weaken the $M–N_2$ π-bond. The two lowest absorption bands which appeared as shoulders in the electronic absorption spectra of *1* and *3*, when run at low temperature, have been assigned to LF transitions ($A_1 \rightarrow {}^{1,3}E$) [13, 20]. The remaining bands in the near ultraviolet region of *1* and *3* have been assigned to MTLCT transitions: two M → P(π) and a M → $N_2(\pi^*)$ [13, 15, 20, 21]. The electronic absorption spectra of *1* and *3* were very similar [13]. However, the room temperature spectrum of *2* was significantly different. Firstly, the two lowest energy LF absorptions appeared as isolated bands, although at similar positions as the corresponding bands of *1* and *3*. Secondly, the M → P(π) CT absorption bands were blue shifted and thirdly, the M → $N_2(\pi^*)$ CT absorption band was red shifted; both observations were consistent with behavior expected of a more basic phosphine.

Considering compound *1* first, irradiation at 436 nm will populate one of the LF states and a Mo → P (${}^{1,3}E$) state (although the absorbance at this wavelength is relatively small). However, 366 nm corresponds closely to the maximum (see Table I) associated with the same MTLCT transition, while 313 nm corresponds closely to a maximum associated with the Mo → N_2 MTLCT transition (see Table I). Clearly, the MTLCT bands are not behaving as effective internal filters of the LF transitions. The small increase in quantum yields with decreasing wavelength could arise as a result of intersystem crossing from states with increasingly larger transition probabilities. Alternatively, depopulation of the e orbital set [Mo → P; $A_1 \rightarrow E(b_2^2e^3a_2^1)$ and Mo → N_2; $A_1 \rightarrow A_2(b_2^2e^32e^1)$] weakening Mo-$N_2$ π-bonding may cause significant bond weakening. Interestingly, irradiation at 546 nm just catches the red tail of the electronic absorption spectrum of *1* where significantly more exchange occurs than in the dark.

The near constancy of the data for compounds *2* and *3* suggests similar M–N_2 bond strengths. The invariance of the quantum yield data with the wavelength of light is surprising (as is the small change observed for compound *1* [22]) considering the enormous variation in absorbance at the different wavelengths. It would be extremely fortuitous if a balance between population of upper excited states, intersystem crossing and radiationless transitions should lead in all cases to an equal concentration of one excited state, *e.g.*, ${}^3E$, a vibrationally 'hot' ground electronic state or some combination of states from which N_2 is lost. If any of the CT states had been active towards N_2 dissociation a change in quantum yield would have been expected since in two cases (313 and 366 nm) the irradiating light was of very similar wavelength at the CT absorption bands. Interestingly, both compounds *2* and *3* are transparent at 546 nm at concentrations of 10^{-3} *M*, and no exchange was observed at that wavelength. The differences in quantum yields between *1*, and *2* and *3* can be explained if it is assumed that the order of activation energies for photodissociation of N_2 in compounds *1*, *2* and *3* is the same as that for their thermal (dark) dissociation, namely; *1* < *2 3*.

Based upon current theories, all that would be needed to cause photodissociate of N_2 from these types of *trans*-bis(N_2) complexes would be population of the ${}^{1,3}E$ state. The data in this Communication do allow us to unambiguously say that photodissociation can occur as a result of populating the lowest excited (LF) state. However, it does not prove that photodissociation cannot arise from other excited states. Further work is in progress to try and provide more definitive answers to these very interesting questions.

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