

## Photochemistry of Planar Four-Coordinate Palladium(II) Complexes. I. The Sterically Hindered Nitro(4-methyl-1,1,7,7-Tetraethyldiethylenetriamine)- palladium(II) Complex Ion

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
*The photochemical behaviour of [Pd(MeEt<sub>4</sub>dien)-NO<sub>2</sub>]<sup>+</sup> (MeEt<sub>4</sub>dien = 4-methyl-1,1,7,7 tetraethyldiethylenetriamine) in methanol solution has been investigated. Under irradiation of different wavelengths corresponding mainly to CT and LF bands of the complex, the initial N-bonded Pd-NO<sub>2</sub> compound undergoes a linkage photoisomerization to Pd-ONO which in turn reacts photochemically and thermally with the solvent to give the final solvo-derivative [Pd(MeEt<sub>4</sub>dien)solv.]<sup>++</sup>. The quantum yields of the two photoreactions, the isomerization and the solvolysis, decrease with decreasing energy of the exciting radiations. A mechanism for both photo-processes is proposed.*


### Introduction

In the area of the photochemistry of coordination compounds, the attention to heavier transition-metal complexes is relatively recent and most of the available information refers to complexes of ruthenium, rhodium, iridium and platinum [1, 2]. In particular, very little is known on the photochemical behaviour of palladium(II) compounds [1] which by way of contrast have been mostly studied thermally [3, 5].

This paper reports a photochemical investigation of the cationic palladium(II) complex [Pd(MeEt<sub>4</sub>dien)NO<sub>2</sub>]<sup>+</sup> in methanol solution. The solvolysis of the same complex was proved to be acid-assisted [6] whilst that of the analogous halide compounds metal-ion-catalyzed [7].

The experimental results support the hypothesis that the irradiation causes the ambidentate ligand

NO<sub>2</sub><sup>-</sup> in the complex to switch from Pd-N  to the

linkage isomer Pd-O  which is the main responsible of the subsequent thermal and photochemical reaction to the final solvo-derivative.

### Experimental

#### Materials

[Pd(MeEt<sub>4</sub>dien)NO<sub>2</sub>]PF<sub>6</sub>, [Pd(dien)NO<sub>2</sub>]NO<sub>3</sub> (dien = diethylenetriamine), [Pd(Et<sub>4</sub>dien)NO<sub>2</sub>]NO<sub>3</sub> (Et<sub>4</sub>dien = 1,1,7,7-tetraethyldiethylenetriamine), were obtained following essentially the literature methods [6–8].

All the compounds were isolated as stable N-bonded species and characterized by elemental analysis; bonding assignments were based on infrared or electronic spectral data [10]. Geometry and bonding of nitro group in [Pd(dien)NO<sub>2</sub>]NO<sub>3</sub> and [Pd(Et<sub>4</sub>dien)NO<sub>2</sub>]NO<sub>3</sub> have already been reported [11, 12]. The molar conductivities in methanol at 18 °C are in the range 80–100 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> and consistent with those of 1:1 electrolytes [13]. Methanol was of spectroscopic grade. All chemicals used were commercial products of reagent grade.

#### Apparatus

The light sources and general equipment to obtain the radiations at desired wavelength were the same as previously described [14]. The intensity of the incident light measured by a ferric oxalate actinometer [15] was of the order of 10<sup>-7</sup> N h ν/min. Spectrophotometric measurements in the u.v. region were performed with an Optica CF 4 R or a Beckman D.U. spectrophotometer, both equipped with a thermostated cell compartment. The infrared spectra were recorded as nujol mulls on a Perkin-Elmer Mod. 457 spectrometer using a polystyrene film for calibration.

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### Procedures

Methanol solutions of the complexes in the range of concentration  $10^{-3}$ – $10^{-4}$  M, were irradiated at 25 °C in standard spectrophotometric cells, under magnetic stirring and periodically taken to the spectrophotometer for recording. The kinetics of the photochemical and thermal reactions were followed in the suitable absorption region. Preliminary experiments performed by purging the solutions with nitrogen gave identical results.

### Results and Discussion

The methanol solutions of  $[\text{Pd}(\text{MeEt}_4\text{dien})\text{NO}_2]^+$  were irradiated at six different wavelengths corresponding to the regions of the ligand CT and LF transitions, namely at 254, 313, 333, 365, 405, 436 nm. An examination of the u.v. spectra (Fig. 2, Table I) shows that at higher energies the first intense CT band ( $\lambda_{\text{max}} = 272$ ) is overlapped by that of the internal ligand transitions: at lower energies, the band related to the ligand field transition ( $\lambda_{\text{max}} \approx 370$ ) is partially masked by the CT band and appears only as a shoulder.

TABLE I. Absorption Maxima of  $[\text{Pd}(\text{MeEt}_4\text{dien})\text{NO}_2]^+$ ,  $[\text{Pd}(\text{MeEt}_4\text{dien})\text{ONO}]^+$  and  $[\text{Pd}(\text{MeEt}_4\text{dien})\text{solv.}]^{++}$  Ions in Methanol Solution.

Complex	$\lambda_{\text{max}}$ (nm)	$\epsilon_{\text{max}}$ ( $\text{cm}^2 \text{mol}^{-1}$ )
$[\text{Pd}(\text{MeEt}_4\text{dien})\text{NO}_2]^+$	272	7200
$[\text{Pd}(\text{MeEt}_4\text{dien})\text{ONO}]^+$	290	10850
$[\text{Pd}(\text{MeEt}_4\text{dien})\text{solv.}]^{++}$	338	1380

Under all the excitations two photochemical processes can be evidenced: the formation of an intermediate species and the subsequent reaction of this species to yield the final solvo derivative. In the early time of irradiation (Figure 1) the constancy of a well defined isobestic point at 278 nm is indicative of the presence of only two absorbing species: the starting nitro compound and the forming intermediate. Late in the irradiation, the solvolytic path becomes significant and a failure of absorbance values to maintain the isobestic point can be observed. On continuing the irradiation, the appearance and the persistence of a new isobestic point at 258 nm, till the end of the reaction, can be related to the presence of the intermediate species and the solvo derivative, the final spectrum being relative to the complex  $[\text{Pd}(\text{MeEt}_4\text{dien})\text{solv.}]^{++}$  [6–7].

It must be noted that the intermediate reacts with the solvent thermally also. In fact, on stopping the irradiation after a period of time in which the Pd-NO<sub>2</sub> has been completely or nearly transformed into

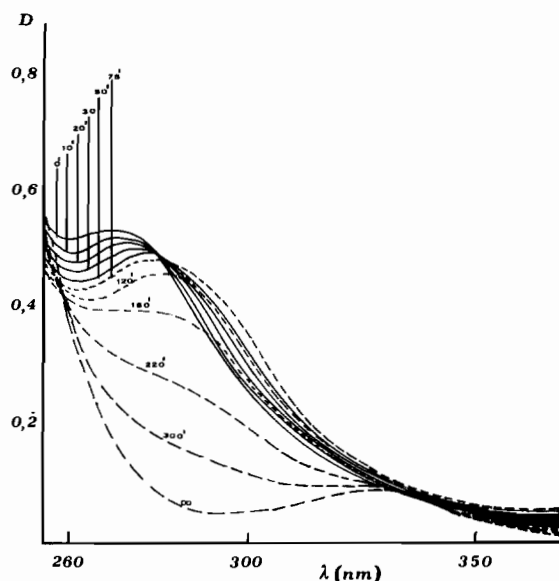


Figure 1. Spectral changes of  $[\text{Pd}(\text{MeEt}_4\text{dien})\text{NO}_2]^+$  in methanol solution. Numbers refer to the irradiation time in minutes.  $\lambda_{\text{irr.}} = 333$  nm;  $[\text{Pd}(\text{MeEt}_4\text{dien})\text{NO}_2]\text{PF}_6 = 7.5 \times 10^{-5}$ .

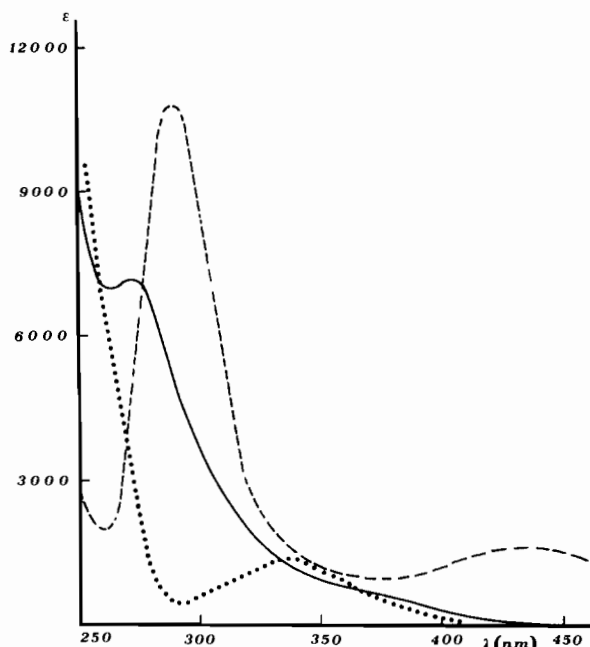


Figure 2. Absorption spectra of  $[\text{Pd}(\text{MeEt}_4\text{dien})\text{NO}_2]^+$  (—),  $[\text{Pd}(\text{MeEt}_4\text{dien})\text{ONO}]^+$  (---), and  $[\text{Pd}(\text{MeEt}_4\text{dien})\text{solv.}]^{++}$  (·····) in methanol solution.

the intermediate, the subsequent solvolytic path takes place in the dark.

The specific rate constant  $k_s$  at 25 °C, obtained for the spontaneous solvolysis of this species is  $4 \times 10^{-5} \text{sec}^{-1}$ . By using this value and the stoichiometric equation relating the total absorbance values to the

extinction coefficients of the two species present in solution, the absorption spectrum of the intermediate could be evaluated (Figure 2).

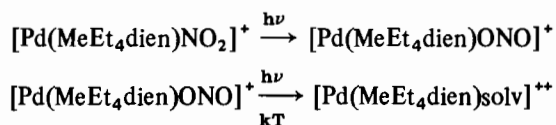
On the basis of the i.r. and u.v. spectra it is not unreasonable to suppose that the intermediate species is the linkage isomer  $[\text{Pd}(\text{MeEt}_4\text{dien})\text{ONO}]^+$ . Goodgame and Hitchman have summarized [17] the behaviour of the infrared bands related to the various modes of bonding of the  $\text{NO}_2$  groups. In particular, as far as the nitro and nitrito complexes of nickel(II) are concerned, the general effect of coordination via nitrogen is to increase both  $\nu_{\text{as}}$  and  $\nu_{\text{s}}$  frequencies with respect to the free ion values at 1328 and 1260  $\text{cm}^{-1}$  respectively, while that of coordination via oxygen is to raise  $\nu_{\text{as}}$  and to lower  $\nu_{\text{s}}$ .

In our case, the i.r. spectra in nujol of the solid obtained by evaporation of the solvent from solutions of  $[\text{Pd}(\text{MeEt}_4\text{dien})\text{NO}_2]^+$  in the same stage of irradiation, as checked by the presence of the isosbestic point, always showed the stretching frequencies of the nitro group at 1370 and 1330  $\text{cm}^{-1}$  [10] together with two weak bands in the region reported [18–21] as characteristic of M–ONO linkage. The  $\nu_{\text{as}}$  appears partially obscured by the nujol band. The uncertainty in the assignment of the nitrito bands can be due to the low concentration of this compound in the mixture, coupled with the possibility of some reisomerization in the solid state which cannot be excluded. Obviously, the need to use methanol as solvent prevents the possibility of observing the isomerization process by monitoring the i.r. spectra during the irradiation. All attempts to obtain a solid mixture in the later stage of irradiation were unsuccessful and consequently the i.r. spectra could not be run.

The observed changes in the u.v. spectra (Fig. 2) further support these findings; in fact the shift to longer wavelengths of CT bands is that predicted for a  $M \rightarrow L$  transition [22, 23] while that of LF bands is in agreement with the relative positions of the two nitro–nitrito ligands in the spectrochemical series [24].

Because of this evidence we lean towards a linkage photoisomerization process in the first stage of irradiation.

Summing up, the overall photochemical process of  $[\text{Pd}(\text{MeEt}_4\text{dien})\text{NO}_2]^+$  can be accounted for by the reaction sequence:



which involves the photosolvation only when the light absorbed by the nitrito isomer becomes competitive with that of the initial compound.

The values of the quantum yields of the photoisomerization process (Table II) as well as those of photosolvolytic (Table III), calculated by applying

TABLE II. Quantum Yield Values for the Linkage Photoisomerization of  $[\text{Pd}(\text{MeEt}_4\text{dien})\text{NO}_2]^+$  at Various Wavelengths of Irradiation.

$\lambda_{\text{exc.}}$ (nm)	$\phi^a$
254 (IL, CT)	0.068
313 (CT, d–d)	0.063
333 (d–d, CT)	0.051
365 (d–d, CT)	0.035
405 (d–d)	0.017
436 (d–d)	0.01

<sup>a</sup>Estimated error  $\pm 5\%$ .

TABLE III. Quantum Yield Values of the Photosolvolytic of  $[\text{Pd}(\text{MeEt}_4\text{dien})\text{ONO}]^+$  at Various Wavelengths of Irradiation.

$\lambda_{\text{exc.}}$ (nm)	$\phi^a$
313 (CT)	0.030
365 (d–d, CT)	0.023
405 (d–d, CT)	0.020
436 (d–d)	0.015

<sup>a</sup>Estimated error  $\pm 5\%$ . Values corrected for the contribution of the thermal process.

the usual suitable equations [25], clearly indicate that they are independent of the initial concentration but dependent on the wavelength of the irradiation.

As far as the unhindered  $[\text{Pd}(\text{dien})\text{NO}_2]^+$  compound is concerned, preliminary experiments seem to indicate that the two photochemical reactions, the isomerization and the solvolysis, are again involved. In this case, owing to the fact that Pd– $\text{NO}_2$  bonding is strongly favoured [23, 26], the rate of the photoisomerization process probably is lower than that of the subsequent photosolvolytic; the consequent presence of more than two species makes it difficult to follow quantitatively the photoreactions.

Qualitative data on the  $[\text{Pd}(\text{Et}_4\text{dien})\text{NO}_2]^+$  complex show that this compound exhibits a photochemical behaviour which is intermediate between that of the more sterically hindered  $[\text{Pd}(\text{MeEt}_4\text{dien})\text{NO}_2]^+$  and the unhindered  $[\text{Pd}(\text{dien})\text{NO}_2]^+$ .

Considering the photochemical mechanism related to the isomerization process, two features are of interest: i) under all the irradiations examined, the same photoreaction occurs and ii) the quantum yields decrease regularly with decreasing energy of excitation (Figure 3). These results are consistent with a mechanism involving a photoreactive excited state as precursor of the reaction. On the other hand, the absence of a concurrent photosolvation of the starting Pd– $\text{NO}_2$  substrate makes the participation of a vibra-

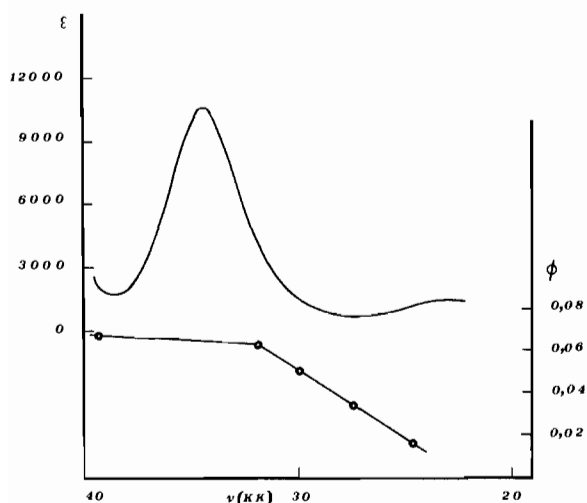


Figure 3. Absorption spectrum of  $[\text{Pd}(\text{MeEt}_4\text{dien})\text{ONO}]^+$  (left scale) and photoisomerization quantum yields (right scale) of  $[\text{Pd}(\text{MeEt}_4\text{dien})\text{NO}_2]^+$ .

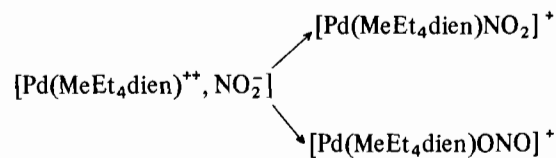
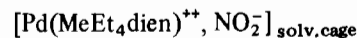
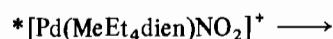
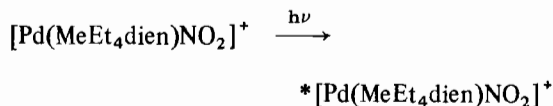
tionally hot ground state unlikely. The circumstance that the nature of this photoreaction does not depend on the specific state attained by direct absorption of the light can be explained taking into account that the different absorbing bands overlap and consequently an efficient communication between the CT and LF state manifolds occurs.

It is to be noted [27, 28] that an unambiguous distinction of the character of the excited states is not to be expected in the complexes of heavier metals.

As far as the nature of the excited state responsible for the linkage isomerization is concerned, it can be assumed that it is a ligand field state. The excitation would cause a weakening of Pd-N bond with a consequent release of the ligand and favour the easy formation of the intermediate ion pair  $[\text{Pd}^{++}, \text{NO}_2^-]$ . The pathway leading to Pd-ONO isomer could be attributed to a recombination process within the ion pair (geminate recombination), the only competitive reaction being the return to Pd-NO<sub>2</sub>. External species (solvent molecules or NO<sub>2</sub><sup>-</sup>) are not involved in the reaction as supported by the lack of a direct solvation and by the fact that the photochemical process is unaffected by adding NO<sub>2</sub><sup>-</sup>.

The trend of quantum yields variation is in agreement with such a mechanism. In fact it depends on the light energy absorbed in excess of that necessary for the release of the ligand; the excess determines the rotation of the NO<sub>2</sub> group to some extent and then the possibility of isomer formation.

The isomerization process can be accounted for by the following scheme:



For the proposed mechanism it is not essential to establish whether the excited states are triplets or singlets. On the other hand, experiments carried out using biacetyl as a triplet donor and ferrocene as quencher indicated that the triplet states are not implied in the process.

In discussing the photosolvation of the formed nitrito isomer, taking into account the analogy between the thermal and the photochemical processes and the lack of some reversion to the nitro isomer, it is reasonable to propose a simple mechanism which implies as precursor a vibrationally hot ground state reached by a non-radiative deactivation of CT and LF states.

The solvolytic process can proceed from this state with a mechanism identical to the thermal one only when its rate is competitive with that of vibrational deactivation. In addition, the quantum yields for a process which occurs through such a pathway should be dependent on the energy of the absorbed light.

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