LASER PHOTOLYSIS STUDIES OF CHLORO(TETRAPHENYLPORPHYNATO)CARBONYLRHODIUM(III) IN BENZENE SOLUTIONS. PHOTO-INDUCED DECARBONYLATION AND TRIPLET FORMATION

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Laser photolysis studies of chloro(tetraphenylporphynato)carbonylrhodium(III) in benzene solutions revealed that the triplet formation, photo-induced decarbonylation, and the isomer formation occur within 20 ns after the laser pulse. Only the triplet yield was found to be dependent on the laser excitation wavelengths (532 and 355 nm).

1. Introduction

Natural carbonylmetalloporphyrins such as carbonylhemoglobin have been well established to undergo facile photo-induced decarbonylation [1–3]. Since the hemoglobin and CO molecules produced by photolysis recombine to regenerate carbonylhemoglobin, the association processes of CO and hemoglobin have been extensively studied by the laser photolysis of carbonylhemoglobin. A few studies, on the other hand, have been reported on the photo-induced decarbonylation of synthetic metalloporphyrins [4,5]. For example, ruthenium(II)carbonyletioporphyrin pyridinate was found to release CO upon visible or UV light irradiation, resulting in the quantitative formation of the dimer of ruthenium(II)-etioporphyrin pyridinate [4].

Recently, photo-induced decarbonylation of organometallics has become an increasingly important subject of photochemistry in relation to catalytic reactions of metal carbonyl compounds [6–8]. In the present study, we have carried out the laser photolysis of chloro(tetraphenylporphynato)carbonylrhodium(III) (ClTPPRh(III)(CO)) in benzene solutions. The photochemistry of ClTPPRh(III)(CO) is considered to provide useful information on the photo-induced decarbonylation of metalloporphyrins as well as metal carbonyl compounds.

2. Experimental

Chlororhodium(III)tetraphenylporphyrin, ClTPPRh(III), was prepared and purified according to the literature [9]. Carbon monoxide gas (99.9%) from Nippon Sanso Ltd. was used as supplied. Reagent grade benzene was used without further purification. A benzene solution of ClTPPRh(III) was bubbled with CO gas to prepare the solution of ClTPPRh(III)(CO). Concentrations of the sample solutions were of the order of 10^{-4} M.

The optical absorption spectra were measured with a Hitachi 330 spectrophotometer. The monochromatic light source for the steady light photolysis was a xenon lamp incorporated in a Hitachi MPF 4 spectrofluorimeter.

The laser photolysis studies were carried out by using a Nd–YAG laser (model HY 500 from J. K. Lasers Ltd.) equipped with second-, third-, and fourth-harmonic generators. The second (532 nm) and third (355 nm) harmonics were used throughout this study. The detection system of the transient spectra were described in an earlier paper [10].

3. Results and discussion

Fig. 1 shows the absorption spectrum of ClTPPRh(III)

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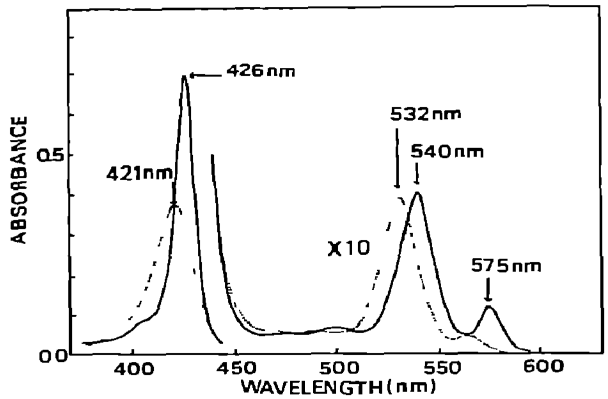

Fig 1. Optical absorption spectra of ClTPPRh(III) (. .) and ClTPPRh(III)(CO) (——) in benzene solutions.

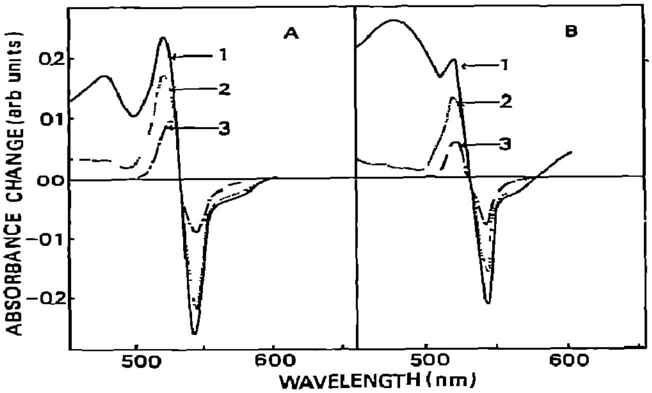

Fig 2. Transient absorption spectra observed after (A) the 355 nm and (B) the 532 nm laser pulses: 1, at 20 ns; 2, at 1 μs; 3, at 10 μs

in benzene solution. The absorption peaks are located at 421, 532, and 563 nm. When the benzene solution of ClTPPRh(III) was bubbled with CO gas, the color of the solution turned from orange to pink owing to the formation of ClTPPRh(III)(CO) [11]:

$$\mathrm{ClTPPRh(III) + CO \rightarrow ClTPPRh(III)(CO)}.$$

The absorption spectrum observed for the benzene solution of ClTPPRh(III)(CO) exhibits peak maxima at 426, 540, and 575 nm as shown in fig. 1. The marked difference in the absorption spectra between ClTPPRh(III) and ClTPPRh(III)(CO) suggests that the electronic bands of ClTPPRh(III) have a charge-transfer (from ligand to central Rh atom) character as in the case of other metalloporphyrins in which d-orbital energy levels of the central metal are close to the porphyrin π level [12]. Presumably, coordination of a CO molecule changes the d-orbital energy levels of the Rh atom in ClTPPRh(III), resulting in the variation of the location of the electronic bands having charge-transfer character.

Photochemical reaction of ClTPPRh(III)(CO) in a benzene solution saturated with CO gas at 1.0 atm was studied by monochromatic steady light irradiation. No spectral changes were observed for the solution upon irradiation at 355 and 532 nm. Furthermore the degassed benzene solution of ClTPPRh(III)(CO) gave no spectral change upon irradiation. Therefore, CO and ClTPPRh(III), if produced by photolysis of ClTPPRh(III)(CO), undergo a recombination reaction to regenerate the parent molecule irrespective of the presence or absence of CO molecules in the bulk solvent. This consideration is supported by laser photolysis studies of ClTPPRh(III)(CO) in benzene solutions, as described later.

Fig. 2A shows the transient absorption spectra observed in the 355 nm laser photolysis of ClTPPRh(III)(CO) in benzene solution saturated with CO gas at 1.0 atm. The spectrum measured 20 ns after the laser pulse shows two positive peak maxima at 475 and 520, and a negative one at 540 nm. The negative absorbance in the spectrum can be undoubtedly ascribed to bleaching of ClTPPRh(III)(CO) in the ground state. At 1.0 μs after the laser pulse, the spectrum exhibits a positive peak at 520 nm and a negative one at 540 nm. The transient spectra disappeared completely within 3 ms after the laser pulse.

The decay analysis of the transient spectra was carried out in order to obtain further information on the transient species. The absorbance change observed at 475 nm was found to follow first-order kinetics with a rate constant of 5.0×10^6 s^{-1}. The decay of the absorbance at 520 or 540 nm was expressed by two exponential functions of time: the first-order rate constants are 3.5×10^5 and 1.6×10^3 s^{-1}. From these results, we consider that three transient species are produced by the laser photolysis of ClTPPRh(III)(CO): species A has an absorption peak at 475 nm with the decay rate of 5.0×10^6 s^{-1}, and the other two, B and C, have the same absorption peak at 520 nm with different rate constants, 3.5

$\times 10^5$ and 1.6×10^3 s^{-1}, respectively. The transient spectrum of the species A was demonstrated to be very similar to the triplet–triplet absorption spectrum of ClTPPRh(III) in benzene solution: the triplet state of ClTPPRh(III) was found to have an absorption peak at 470 nm and a first-order rate constant of 5.6×10^4 s^{-1}. From this result we consider that species A can be ascribed to the photo-excited triplet state of ClTPPRh(III)(CO). It is likely that an axial CO molecule gives only weak effects on the triplet–triplet absorption spectrum. The fact that the triplet lifetime of ClTPPRh(III)(CO) is markedly shorter than that of ClTPPRh(III) suggests the increase in the non-radiative decay rate constant of the triplet state by axial coordination of a CO molecule.

The transient absorption spectra measured at 1.0 and 10 μs shown in fig. 2A are found to be in good accord with the difference spectrum obtained by subtracting the absorption spectrum of ClTPPRh(III) from that of ClTPPRh(III)(CO).

The laser photolysis studies of ClTPPRh(III)(CO) in a N_2-saturated benzene solution revealed that: (1) the transient spectrum observed immediately after the pulse is the same as that observed for the CO-saturated solution of ClTPPRh(III)(CO), (2) the transient species A and B decay according to first-order kinetics: the rate constants are in agreement with those obtained with the laser photolysis of ClTPPRh(III)(CO) in a CO-saturated benzene solution, and (3) species C, on the contrary, decays according to second-order kinetics· the apparent bimolecular rate constant k_b/ϵ (ϵ is the molar absorption coefficient of the transient C at 520 nm), was determined to be $k_b/\epsilon = 4.8 \times 10^2$ M^{-1} s^{-1}. On the basis of the above findings, species C is concluded to be ClTPPRh(III) which reacts with CO to regenerate ClTPPRh(III)(CO).

The first-order rate constant of species B is found to be independent of the presence or absence of CO molecules in the solution. Judging from the first-order decay, we assume that species B has an isomeric structure of ClTPPRh(III)(CO). From the decay analysis of the transient spectrum at 475, 520, and 540 nm, species A, B, and C are concluded to be produced within the duration of a laser pulse.

Fig. 2B shows the transient absorption spectra observed in the 532 nm laser photolysis of ClTPPRh(III)(CO) in a CO-saturated benzene solution. The spectrum measured 20 ns after the laser pulse differs markedly from that observed in the 355 nm laser photolysis. However, the spectra taken at 1.0 and 10 μs are very similar to those observed in the 355 nm laser photolysis. The decay analysis of the transient spectra reveals that three transients, A, B, and C, which were characterized earlier, are also produced by the 532 nm laser photolysis. A significant difference between the transient spectra measured at 20 ns after the 355 and the 532 nm laser pulse indicates that the relative yields of these species depends on the excitation wavelength.

The ratio of the quantum yield for the formation of species i (i = A, B, and C) obtained by a 532 nm laser flash to that by a 355 nm laser flash, $\Phi_i(532\ \text{nm})/\Phi_i(355\ \text{nm})$, is calculated from the absorbance changes in the transient spectra and the number of photons, I_{abs}, absorbed by ClTPPRh(III)(CO): I_{abs} is evaluated by measuring the absorption intensity of the triplet zinc(II) tetraphenylporphyrins, Zn(II)TPP, in benzene solutions after the 355 and 532 nm laser pulses. On the assumption that the triplet yield of Zn(II)TPP is independent of the excitation wavelength, the values of $\Phi_i(532\ \text{nm})/\Phi_i(355\ \text{nm})$ are evaluated as

$$\Phi_A(532\ \text{nm})/\Phi_A(355\ \text{nm}) = 1.43 \pm 0.05,$$

$$\Phi_B(532\ \text{nm})/\Phi_B(355\ \text{nm}) = 1.05 \pm 0.05$$

and

$$\Phi_C(532\ \text{nm})/\Phi_C(355\ \text{nm}) = 1.05 \pm 0.05.$$

The absorbance changes used for the calculation of $\Phi_i(532\ \text{nm})/\Phi_i(355\ \text{nm})$ were measured at 460 nm for i = A and at 520 nm for i = B and C. The results described above demonstrate that the yield of formation of the triplet ClTPPRh(III)(CO) is dependent on the excitation wavelength. However, the yields for the photo-induced decarbonylation as well as the formation of species B seem to be independent of excitation wavelength. The marked difference between the transient spectra observed 20 ns after the 532 and the 355 nm laser pulses is considered to arise from the wavelength dependence of the yields, Φ_{st}, for the formation of triplet ClTPPRh(III)(CO).

It is well recognized that the higher excited states, S_n ($n > 1$), of organic molecules in solution are readily relaxed to form the lowest excited singlet state, S_1, with an efficiency of unity [13]. Since the lowest excited singlet state undergoes intersystem crossing to yield the lowest triplet state, the yield of triplet formation, Φ_{st}, is known to be independent of the excitation wavelength. The present results, however, show a marked dependence of Φ_{st} on the laser excitation wavelength. The absorption spectrum of ClTPPRh(III)(CO) has two major bands, the Q band (S_1) at 540 nm and the Soret band (S_2) at 426 nm. The 532 and 355 nm laser pulses, therefore, are considered to be absorbed by the S_1 and the S_n ($n \geqslant 2$) band, respectively. On the basis of $\Phi_{st}(532\ \text{nm})/\Phi_{st}(355\ \text{nm}) = 1.43 \pm 0.05$, we assume that the internal conversion process, S_n ($n \geqslant 2$) $\rightarrow S_1$, is a highly inefficient process in the excited states of ClTPPRh(III)(CO). This assumption leads to the conclusion that: (1) a 355 nm laser pulse produces the triplet state, T_1, of ClTPPRh(III)(CO) according to the process: S_n ($n \geqslant 2$) $\rightarrow T_n \rightarrow T_1$, where T_n is a higher excited triplet state, (2) the triplet formation by the 532 nm laser pulse is described as $S_1 \rightarrow T_1$, and (3) photodecarbonylation and the formation of a ClTPPRh(III)(CO) isomer take place both in the S_n ($n \geqslant 2$) and S_1 states.

4. Conclusion

Three transient species are produced by the laser photolysis of ClTPPRh(III)(CO) in benzene solutions: (1) a photo-excited triplet state of ClTPPRh(III)(CO), (2) ClTPPRh(III) formed by photodecarbonylation of ClTPPRh(III)(CO), and (3) an isomer of ClTPPRh(III)(CO). The transient spectrum measured 20 ns after the 355 nm laser pulse is found to differ markedly from that observed after the 532 nm laser pulse. This fact is interpreted by the wavelength dependence of the yields of formation of triplet ClTPPRh(III)(CO). The decay analysis of the transient spectra confirms that neither photo-induced decarbonylation nor the formation of the isomer of ClTPPRh(III)(CO) occurs from triplet ClTPPRh(III)(CO) Further studies are necessary to identify the molecular structure of the isomer.

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