Photogeneration of Monomeric Porphyrins from the (tetraphenylporphyrin)Rh−In(octaethylporphyrin) Dissociation of the Rh−In Bond: Investigation of Their Reactions in the Picosecond−Microsecond Time Domain

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Introduction

Literature reports show that a number of Rh−In heteroporphyrin dimers are thermally stable in hydrocarbon solvents but undergo photodissociation into mononuclear porphyrin products when exposed to visible light.[1−3] The photochemically generated monomers are very reactive toward alkyl halides, e.g., RX in eq 1, producing mononuclear porphyrins with axially

$$(Por)Rh-In(Por') + RX \xrightarrow{h\nu} (Por)RhX + (Por')InX \quad (1)$$
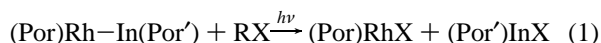
(Por and Por′ are different porphyrin macrocycles)

coordinated halide, e.g., $(Por)M^{III}Cl$ with M = Rh and In. The expected metalloalkyl products, i.e., (Por)MR where R = alkyl, were not detected, and secondary photolysis is a probable reason for their absence.

In contrast to the Rh−In heteroporphyrin dimers, which are thermally stable, Rh(II) or Ir(II) porphyrinato dimers, $[M(Por)]_2$, are much more reactive compounds that participate in numerous organometallic reactions.[4−9] This includes some unusual reactions, i.e., the formation of metalloformyl species, CO reductive coupling, and hydrocarbon activation.[4−12] Radical-like pentacoordinates, $[(OEP)Rh^\bullet]$ where OEP = octaethylporphyrin, were identified in early studies about the insertion and oxidative

addition reactions of $[Rh(OEP)]_2$, eqs 2−4.[13−15] The radical-chain initiation/termination: $[Rh(OEP)]_2 \rightleftarrows 2[Rh(OEP)^\bullet]$

$$(2)$$

chain propagation: $[(OEP)Rh^\bullet] + PhCH=CH_2 \rightarrow$

$$(OEP)RhCH_2C^\bullet HPh \quad (3)$$

$(OEP)RhCH_2C^\bullet HPh + [Rh(OEP)]_2 \rightarrow$

$$(OEP)RhCH_2CH(Ph)Rh(OEP) + [(OEP)Rh^\bullet] \quad (4)$$

like species in eqs 2−4 may have a nature similar to that of intermediates in the photochemical reactions of (Por)Rh−In-(Por′), eq 1. The reactions of such metastable Rh and In porphyrins occurring in a picosecond−microsecond time domain were investigated in this work.

Experimental Section

Flash Photolysis. Two different flash photochemical apparatus were used for the investigations of reaction kinetics and transient spectra in the 20 ps−100 μs time domain. A mode-locked Nd:YAG (Quantel) laser was used for the generation of 20 ps pump (351 nm) and probe (400−700 nm) light pulses.[16] The probe of optical events was set at times ranging from several hundred picoseconds in advance to the pump to several nanoseconds following the pump by means of a computer-controlled optical delay. Photochemically induced changes in the sample's optical density, OD, were recorded with a spectrograph and a dual multichannel analyzer. In this detection system, two spaces inside the reaction cell were probed but only one of them spatially overlapped with the pump. Processes occurring on a longer time scale, i.e., more than several nanoseconds, were investigated with flash photolysis equipment described elsewhere.[17]

Luminescence was investigated on an SLM-Aminco-8100 connected to a DELL 333P microcomputer by procedures described elsewhere.[18]

Solutions for the photochemical work were deaerated with streams of ultrahigh-purity N_2 before and during the irradiations. Concentrations of the complexes were adjusted, i.e., optical densities less than or equal to 0.1 at 355 nm with a 2 mm optical path, to result in homogeneous concentrations of photogenerated intermediates within the volume of irradiated solution. The effect of the added electrolyte on the reaction kinetics was investigated in solutions having 0.01 and 0.001 M tetrabutylammonium perchlorate. Other experiments were conducted without the electrolyte.

Materials. The metal−metal-bonded complexes were available from previous work and were used without further purification.[2,3] The solvents, toluene and dichloromethane, were Aldrich HPLC grade and used without further purification.

Results

Flash irradiations (λ_{exc} 355 nm) of (TPP)Rh−In(OEP), TPP = tetraphenylporphyrin, in deaerated toluene resulted in a

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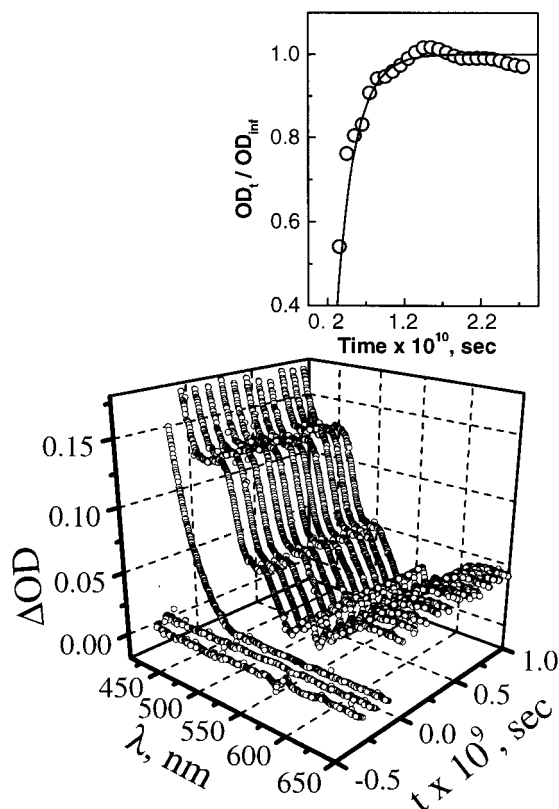(18) Ferraudi, G.; Feliz, M.; Wokan, E.; Moya, S. A.; Guerrero, J. *J. Phys. Chem.* **1995**, *99*, 4929.

Figure 1. Time-resolved spectra recorded when deaerated solutions of (TPP)Rh−In(OEP) in toluene were irradiated at 355 nm. The inset shows the 600 nm optical density change, ΔOD, measured at an instant t, divided by the value, ΔOD_{inf}, determined at the end of the reaction. The solid line was calculated with $\Delta OD_t/\Delta OD_{inf} = (1 - \exp(-kt))$, where $k = 4.1 \times 10^{10}$ s^{-1} is the rate constant that resulted from a least-squares curve fitting of the experimental data.

prompt increase of the optical density (650 nm $\geq \lambda_{ob} \geq$ 420 nm) within the 20 ps laser flash, Figure 1. While the flash-generated optical spectrum undergoes further changes near the 450 nm spectral region over several nanoseconds, a faster growth of the optical density was observed at wavelengths near 600 nm, Figure 1. A curve fitting of the time-resolved 600 nm optical density, inset to Figure 1, suggests that this process is kinetically of first or pseudo first order with a rate constant of $k = 4.1 \times 10^{10}$ s^{-1}.

On a longer time scale, the decay of the flash-generated optical absorptions (650 nm $\geq \lambda_{ob} \geq$ 420 nm) was observed between 1 and 200 μs. A simultaneous recovery of the solution optical density was monitored at wavelengths between 375 and 425 nm. Decay of the optical density in the near-IR does not return to preirradiation values; i.e., the recombination of photogenerated fragments does not regenerate (TPP)Rh−In-(OEP) with a 100% efficiency and allows the formation of new products. The rate of the optical density changes, decay of OD between 650 and 420 nm and recovery between 375 and 425 nm, depends on the respective concentrations of (TPP)Rh−In-(OEP) and photogenerated intermediates. In these experiments, Figure 2, the concentration of photogenerated intermediates was regarded proportional to the optical density change, ΔOD_0, recorded 40 ns after the laser flash irradiation. The recovery of the bleach and the decay of transient optical absorptions are both kinetically second order for relatively low concentrations of the photolyte and nearly independent of added electrolyte. The ratios of the rate constant to the extinction coefficient were dependent on the monitoring wavelength, i.e., k/ϵ = 9.4 $\times$ 10^6 cm/s at λ_{ob} 620 nm and k/ϵ = 7.3 $\times$ 10^6 cm/s at λ_{ob} 470 nm. In
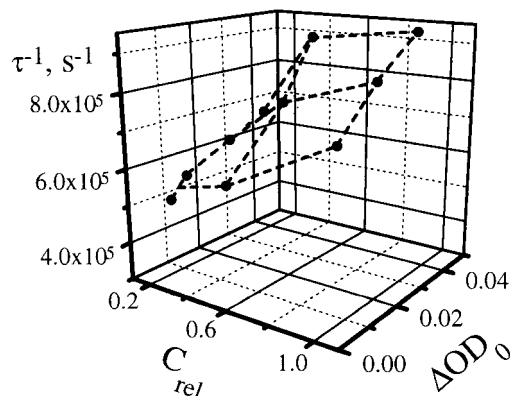

Figure 2. Dependence of the reaction intermediate lifetime on the concentrations of the flash-generated intermediate and (TPP)Rh−In-(OEP). The reaction was followed at 440 nm in 355 nm flash irradiations of (TPP)Rh−In(OEP) in toluene. The flash-induced optical density change, ΔOD_0, is taken as a measure of the flash-generated concentration of monomers. Concentrations of (TPP)Rh−In(OEP) are given relative, C_{rel}, to the maximum concentration, ca. 10^{-5} M, used for the measurements.

accordance with this second-order reaction kinetics, the ratio of the 470 nm to the 620 nm values of k/ϵ is the same ratio of the 620 to the 470 nm optical density changes; i.e., $\Delta_{OD620}/\Delta_{OD470} \sim 1.3 \pm 0.1$ immediately after the laser flash. Departures from the second-order reaction kinetics and a dependence of the rate constant on the (TPP)Rh−In(OEP) concentration were detected with low concentrations of photogenerated intermediates, Figure 2.

While dichloromethane did not react thermally with (TPP)-Rh−In(OEP) within the time (less than several hours) demanded by the 355 nm flash photolysis experiments, it functioned as a scavenger of photoproducts. In solutions of the Rh−In porphyrin with various concentrations of CH_2Cl_2, a bleach of the optical density at 409 nm and a decay of the flash-generated optical density at 470 nm exhibited the same rate. Moreover, such a decay of the 470 nm optical density was kinetically of a pseudo first order with respect to the concentration of photoproducts. The corresponding rate constant, measured under pseudo-first-order reaction conditions, varied with solvent, i.e., toluene or cyclohexane, and exhibited the expected linear dependence on the CH_2Cl_2 concentration, Figure 3.

Similar experimental observations were made in the 355 nm flash photolysis of the related compounds (OEP)Rh−In(TPP) and (TPP)Rh−Tl(OEP).

Discussion

The 365 nm flash irradiations of (TPP)Rh−In(OEP) in toluene show the photogeneration of reaction intermediates in less than 20 ps, namely the time width of the laser pulse. Inspection of the transient spectra, Figure 1, reveals that prompt flash-generated optical absorptions at 600 nm are, in relation to those at 440 nm, much larger than can be expected for the lowest excited state of the porphyrins.[19−21] Also the assignment of such spectra to the lowest excited state provides a dubious rationale for the lack of a perceptible luminescence. On the basis of the observed reaction with CH_2Cl_2, Figure 3, and reported products from steady-state photolysis,[2,3] these primary species are most likely the result of a homolytic dissociation of the Rh−In bond. Spectral transformations with a rate constant

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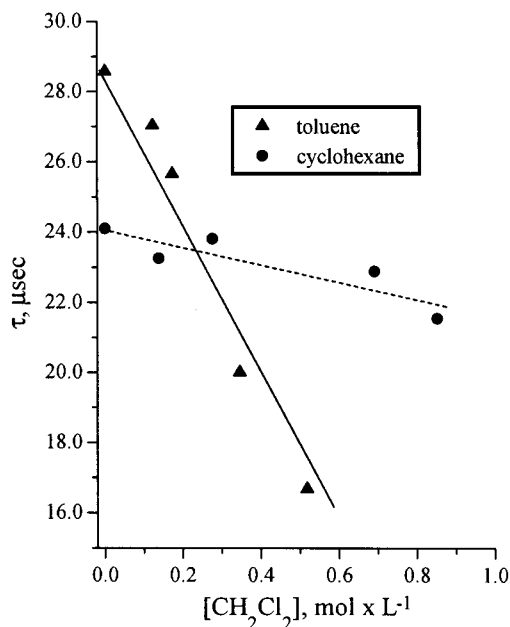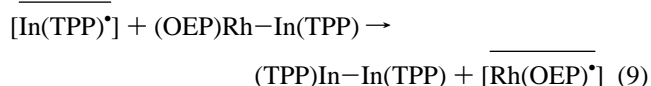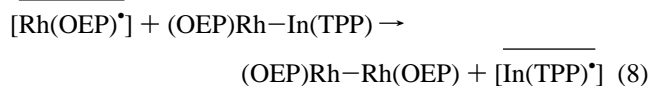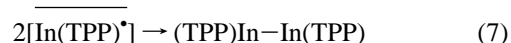(21) Kalyanasundaram, K.; Gratzel, M. *Helv. Chim. Acta* **1980**, *63*, 478.
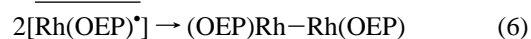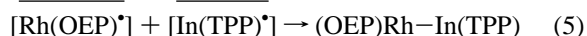
Figure 3. Dependence of the reaction intermediate lifetime on CH$_2$-Cl$_2$ concentration. The reaction was followed at 440 nm in 355 nm flash irradiations of (TPP)Rh—In(OEP) in toluene and cyclohexane, respectively.

$k = 4.1 \times 10^{10}$ M^{-1} s^{-1}, Figure 1, indicate that the primary products undergo transformations that lead to intermediates which are scavenged by CH$_2$Cl$_2$ on a longer time scale, Figure 3. Specific interactions of these scavengeable intermediates with the solvent provide a rationale for the observed differences in their lifetimes, $\tau = 28.7$ μs in toluene and $\tau = 24.1$ μs in cyclohexane, and in their solvent-dependent rates of reaction with CH$_2$Cl$_2$, Figure 3. In this regard, the spectral transformations observed in a subnanosecond time domain, Figure 1, could be the result of reorganizations, nuclear and electronic, and/or solvation processes of the primary products. Indeed, conversions between electronic isomers, i.e., between (por)In(O) and porphyrin radical species, or a unimolecular reorganization of the metal coordination sphere from a square pyramid to a square-planar complex may be processes fast enough to be observed on a subnanosecond time scale. An equally fast process, association of the solvent to the metallo fragments, i.e., to saturate the coordination sphere, also provides a rationale for these fast spectral changes. Similar solvent effects have been observed before in reactions of coordinatively unsaturated transition metal carbonyls.[22]

The dual dependencies of the reaction rate on photoproduct and photolyte concentrations, Figure 2, have to be interpreted in terms of a competition among several reactions, eqs 5−9. In

$$\overline{[Rh(OEP)^{\bullet}]} + \overline{[In(TPP)^{\bullet}]} \rightarrow (OEP)Rh-In(TPP) \quad (5)$$

$$2\overline{[Rh(OEP)^{\bullet}]} \rightarrow (OEP)Rh-Rh(OEP) \quad (6)$$

$$2\overline{[In(TPP)^{\bullet}]} \rightarrow (TPP)In-In(TPP) \quad (7)$$

$$\overline{[Rh(OEP)^{\bullet}]} + (OEP)Rh-In(TPP) \rightarrow$$
$$(OEP)Rh-Rh(OEP) + \overline{[In(TPP)^{\bullet}]} \quad (8)$$

$$\overline{[In(TPP)^{\bullet}]} + (OEP)Rh-In(TPP) \rightarrow$$
$$(TPP)In-In(TPP) + \overline{[Rh(OEP)^{\bullet}]} \quad (9)$$

these equations, the overline in the radical-like photofragments is to indicate that they are not the primary products but intermediates that resulted from the chemical reactions described above, i.e., processes with lifetimes of several hundred picoseconds. Recombination of the photofragments, eqs 5−7, accounts for the second-order dependencies on the monomers' flash-photogenerated concentrations, Figure 2. The observed formation of species, spectroscopically different from the photolyte and stable over several microseconds, suggests that eqs 6 and 7 may play a significant role in early events leading to the terminal products. Equally important to eqs 5−7 appear to be reactions of the photofragments with (TPP)Rh—In(OEP), processes that explain the observed dependence of the reaction rate on the photolyte concentration. Each photofragment can react with the photolyte according to kinetically distinguishable processes, which will make the rate of the reactions dependent on (TPP)Rh—In(OEP) concentration.

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