Studies of the Chemical Oxidation of Ru(II) Complexes of Porphyrins to Form the Corresponding Ru(IV) Complexes

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Abstract

Reactivity of ruthenium porphyrin π-cation radicals of general formula Ru(CO)(porphyrin)$^{\bullet+}$Br (porphyrin: tetraphenylporphyrin, octaethylporphyrin) has been investigated. Ru(CO)TTP (tetra-(*p,m,o*-tolyl)porphyrin) and Ru(CO)OEP were readily oxidized to form respective π-cation radicals, which afforded well resolved, hyperfine shifted NMR spectra. Non-Curie low behaviour for Ru(CO)TTP$^{\bullet+}$-Br was interpreted in terms of thermal equilibrium between $^2A_{2u} \rightleftharpoons {}^2A_{1u}$ π-cation radical states. The π-cation radical heated at 100 °C decomposed. The reaction was followed by NMR spectroscopy. The NMR results indicate that the symmetry of the parent complex is retained after oxidation. The formation of Ru(IV)(porphyrin)Br$_2$ accounts for the process observed. The NMR spectrum is strongly paramagnetically shifted. The dominant π-spin transfer is in accord with the $d_{xy}{}^2d_{xz}{}^1d_{yz}{}^1$ ground state. The new convenient route for generation of monomeric Ru(IV) porphyrins via decarbonylation of π-cation radicals has been established.

Introduction

The use of synthetic porphyrins and metalloporphyrins to model naturally occurring porphyrin systems which are difficult to study directly is well established. Interest has increased recently in ruthenium analogues of their compounds because otherwise reactive intermediates are expected to be more stable for ruthenium than for iron complexes [1]. This is particularly relevant for the studies of metalloporphyrin π-cation radicals which have been suggested as intermediates in a number of natural porphyrin systems [2]. One can expect that the slower kinetics of ruthenium centers would allow better characterization of intermediates.

In this study we describe reactivity of ruthenium porphyrin π-cation radicals of a general formula Ru(CO)TPP$^{+\bullet}$Br. In particular we are interested in a thermally induced decarbonylation process. π-bonding between metal and carbonyl is expected to be weaker in π-cation radicals than in parent ruthenium(II) porphyrin, facilitating removal of the carbonyl group [3].

NMR spectra of paramagnetic metalloporphyrins seem to be very informative concerning electronic structure, spin and ligation states [4]. Recent reports on NMR spectra of paramagnetic ruthenium porphyrins have opened a route for a wider application of NMR in ruthenium porphyrin studies [5–10].

Herein, we report preliminary NMR results of Ru(CO)TPP oxidation with Br$_2$. Products of reactions have been characterized by respective NMR spectra. Detailed analysis of NMR parameters sheds an additional light on their electronic and molecular structure.

Experimental

Tetra-(*p,m,o*-tolyl)porphyrin (Tp,m,oTPH$_2$), tetraphenylporphyrin (TPPH$_2$), d$_8$TPPH$_2$ (pyrrole deuterated), ruthenium(II) carbonyl tetratolylporphyrin and ruthenium carbonyl octaethylporphyrin were synthesized according to the published procedures [11–13]. Octaethylporphyrin (Aldrich) was used as received. Purity of the compounds was checked by NMR and UV–Vis spectroscopies. Oxidation of Ru(CO)TTP to a π-cation radical was performed by an NMR titration of the CDCl$_3$(CD$_2$Cl$_2$, C$_2$D$_2$Cl$_4$) solution of the respective Ru porphyrin with Br$_2$. To facilitate the titration procedure Br$_2$ dissolved in a deuterated solvent was used. The titration was stopped before bromination of the phenyl or pyrrole position could be observed in the NMR spectrum of Ru(CO)TTP. A sample of π-cation radical, prepared as above, was sealed in an NMR tube and was the subject of systematic high temperature studies (up to 100 °C). The reaction progress was followed by NMR. Optical absorption spectral measurements were made on a Specord UV–Vis spectrometer. Proton NMR spectra of 100 MHz were recorded with JEOL-PS-100, Tesla and Nicolet-360

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MHz spectrometers. Proton chemical shifts are referenced to TMS. The sample concentration was 5–10 mM.

Results and Discussion

One electron oxidation of Ru(CO)TTP was accomplished using Br_2 as an oxidizing agent. An appearance of separate resonances of Ru(CO)TPP and its cation radical $Ru(CO)TTP^{+\bullet}Br$ indicate that the rate of electron exchange between these two species is slow ($k < 1.5\ 10^3\ s^{-1}$).

One has to avoid an excess of Br_2 as bromination at pyrrole and phenyl positions competes with the oxidation. The complex multiplets of paramagnetically shifted resonances have been recorded for brominated samples.

Usually, both species, *i.e.* π-cation radical and starting Ru(CO)TTP, were present in comparable concentrations.

The resonance assignment for the $Ru(CO)TTP^{+\bullet}$ cation radicals have been determined by relative areas, line width analysis, specific deuteration and selective methyl substitution (Table I, Fig. 1).

A temperature dependence of isotropic shift was studied. The resonances show linear dependence of a Curie plot (Fig. 2). Extrapolated intercepts ($T^{-1} \rightarrow 0$) do not correspond to positions of respective diamagnetic reference. The salient feature of $^2A_{2u}$ porphyrin π-cation radical is the distribution of a substantial amount of positive spin density at the *meso* carbon and pyrrole nitrogens while the $^2A_{1u}$ radical has a node at the *meso* position but a large spin density at the pyrrole carbon. A correlation exists between the sign of spin density on the *meso* carbon and a phenyl ring spectrum pattern [14]. In the case of positive spin density, the phenyl ring shows upfield shift for *ortho* and *para* and downfield for *meta* resonances when the π-delocalization dominates the shift. The observed spectrum pattern of cation radicals studied follows the spin distribution

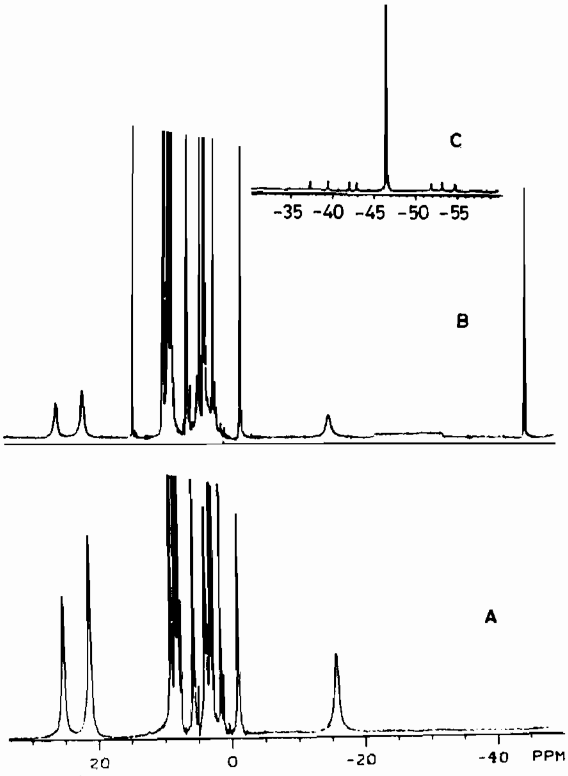

Fig. 1. ^1H NMR spectra of chloroform solution of ruthenium tetratolylporphyrins at 25 °C: (A) $Ru(CO)TpTP^{\bullet+}Br$ π-cation radical; (B) $Ru(IV)(TpTP)Br_2$, (C) pyrrole resonance region of $Ru(IV)(TpTP)Br_2$ to which an excess of bromine has been added. The resonances of diamagnetic Ru(CO)TpTP have been cut off in intensity.

TABLE I. Chemical Shift of Ru Porphyrins[a] (ppm *vs.* TMS in $CDCl_3$, 25 °C)

Compound	Position						
	Pyrrole	*ortho*	*meta*	*para*	*o*-CH_3	*m*-CH_3	*p*-CH_3
$Ru(CO)TPP^{\bullet+}Br$	3.35	−13.43	23.36	−6.01			
$Ru(CO)TpTP^{\bullet+}Br$	2.60	−15.60	23.40				20.20
$Ru(CO)TmTP^{\bullet+}Br$	1.60	−12.91 −14.02	22.95	−6.36		−1.06	
$Ru(CO)ToTP^{\bullet+}Br$	b	−6.69	28.09 24.58	b	12.24		
$Ru(TPP)Br_2$	−47.17	5.27	12.64				
$Ru(TpTP)Br_2$	−44.58	2.78	13.23				8.07
$Ru(TmTP)Br_2$	−46.40	4.19	12.78	5.12		2.17	
$Ru(ToTP)Br_2$	−46.68 −46.98 −47.16	6.90	13.45 12.72	b	4.58		

[a] Ru(CO)TTP was used as a diamagnetic reference. [b] Not observed.

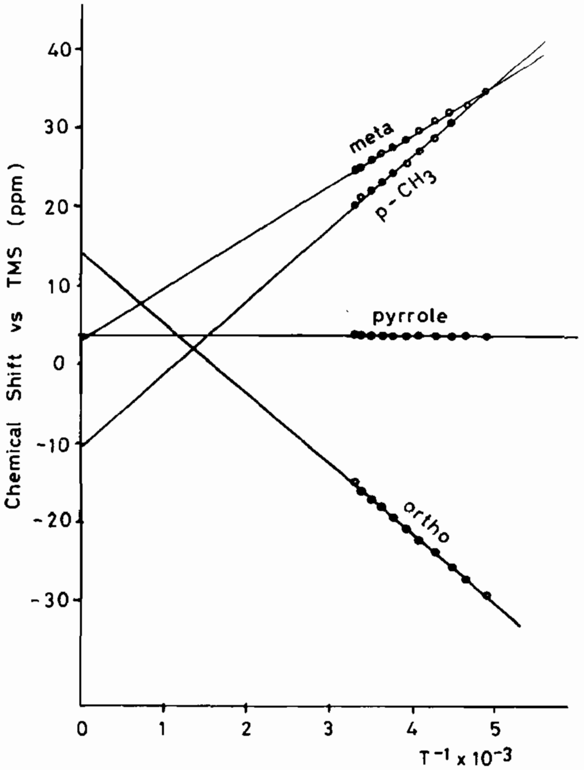

Fig. 2. Temperature dependence of the ^1H NMR spectra of $Ru(CO)TpTPP^{\bullet +}Br$ π-cation radical.

expected for the $^2A_{2u}$ electronic configuration. The observed deviation from the regular Curie law behaviour (positive for *ortho* proton and negative for *meta* and p-CH_3) suggests the thermal equilibrium between two possible electron distributions, *i.e.* $^2A_{2u} \rightleftharpoons {}^2A_{1u}$ [2]. If we assume that the a_{2u} orbital possesses slightly higher energy than the a_{1u} orbital the relative contribution of the $^2A_{2u}$ state increases with increasing temperature to afford less positive spin density at the *meso* position, accounting for the observed deviations. The isotropic shift of phenyl ring protons is realized only via π-interaction of porphyrin and phenyl orbitals. The position of phenyl resonances as well as the contact shift sign reversal after the methyl substitution are consistent with the π-delocalization mechanism.

Under the conditions used in this work the Ru(II) porphyrin cation radical is relatively stable at 25 °C. The π-cation radical samples heated at 100 °C decomposed. The process has been followed by NMR.

A new set of resonances appeared in the course of decomposition (Fig. 1). The reaction is irreversible. The new species is air and temperature stable. However we have not got a pure sample of this material yet. The resonance assignment has been made by standard procedures described for π-cation radicals. One has to note an extremely efficient electron relaxation mechanism as line widths are very small (pyrrole line width 19 Hz at 25 °C). Mirror symmetry in the porphyrin plane is preserved. The *meso* phenyl resonances are recorded as a set of narrow singlets over the entire temperature range studied (−60 to 100 °C). The slow rotation of phenyls usually observed for Ru(CO)TPP [12] is expected for the new species. The simplicity of the spectrum cannot result from any dynamic process but from an intrinsic symmetry of the system, *i.e.* two axial ligands are identical. The coordination of two carbonyl groups is very unlikely in the conditions described, so it is suggested that two Br^- anions occupy the axial positions. The overall appearance of the new intermediate spectrum indicates that it possesses an effective four-fold symmetry and that the porphyrin macrocycle has not degenerated under the conditions of intense heat.

The following reaction can account for the processes observed spectroscopically.

$$2Ru(II)(CO)TTP^{+\bullet}Br \longrightarrow Ru(IV)TTPBr_2 + CO + Ru(CO)TTP$$

At present, we suggest a Ru(IV) oxidation state for the reaction product. As a species of analogous electronic structure has been recently obtained [15] via oxidation of a dimeric $[Ru(OEP)]_2$ compound, we carried out decarbonylation of a $Ru(CO)OEP^{+\bullet}Br$ cation radical in conditions already established for $Ru(CO)TPP^{+\bullet}Br$. The process resulted in an almost quantitative formation of $Ru(OEP)Br_2$ as NMR parameters were very similar to those reported previously [15] (Fig. 3).

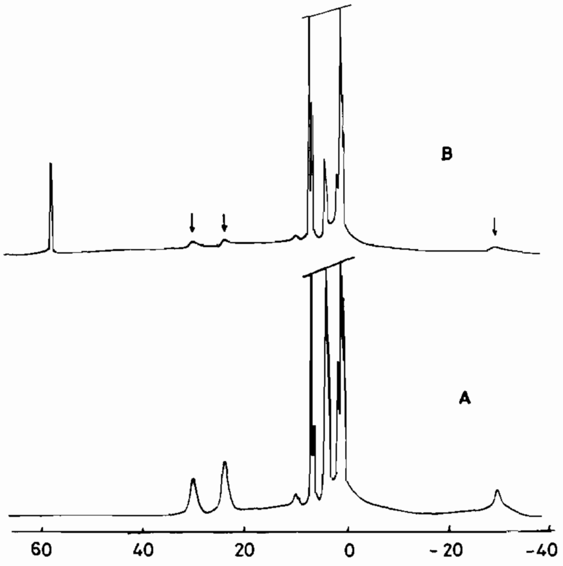

Fig. 3. ^1H NMR spectra of chloroform solution of ruthenium octaethylporphyrins at 25 °C: (A) $Ru(CO)OEP^{\bullet +}Br$; (B) $Ru(IV)(OEP)Br_2$ formed in the decomposition process of $Ru(CO)OEP^{\bullet +}Br$ π-cation radical after heating at 100 °C. Arrows denote residual resonances of π-cation radical.

Hence, we have established a new, convenient route for generation of monomeric Ru(IV) porphyrins via decarbonylation of π-cation radicals. A pyrrole isotropic shift value (Table I) is strikingly different from any metalloporphyrin low spin d^5 system [4]. However a similar isotropic shift has been measured for Fe(IV)TPP(Aryl) [16] where the d^4 electronic structure was definitely established.

As the NMR spectrum of Ru(IV) is paramagnetically shifted, it requires an $d_{xy}{}^2d_{xz}{}^1d_{yz}{}^1$ occupancy in D_{4h} symmetry. The resulting A ground state should exhibit an isotropic *g* tensor. The dipolar contribution exists as a result of anisotropy of the zero field splitting (ZFS). It has a characteristic T^{-2} dependence [4]. The modulation of ZFS by motion of the molecule gives rise to the short T_{1e} and therefore exhibits narrow NMR lines [4].

A plot of the shift data for various resonances of Ru(IV)(TpTP)Br_2 illustrates the curvature (Fig. 4). The fit to the pyrrole experimental points gives a T^{-2} term and an estimation of the dipolar contribution [4, 17]. From the relative geometric factors the dipolar contribution at any other position could be estimated (pyrrole 12.5 ppm; *ortho*-H 6.6 ppm; *meta*-H 3.1 ppm; *meta*-CH_3 1.9 ppm; *para*-H 4.6 ppm; *para*-CH_3 2.0 ppm).

The *meso* aryl shifts were found to be totally consistent with a predominantly π-delocalization mechanism in that the proton and methyl shift are of comparable magnitude but of opposite sign at all ring positions. The π-phenyl π-porphyrin orbital overlap accounts for the spin density transfer. The large upfield contact shift of pyrrole protons and downfield of α-CH_2 protons are indicative of π-spin density transfer to the fully occupied 3e(π) porphyrin molecular orbital from the half filled d_{xz}, d_{yz} orbitals of the metal ion (M → L charge transfer). However, the other available mechanism of π-density transfer acts simultaneously.

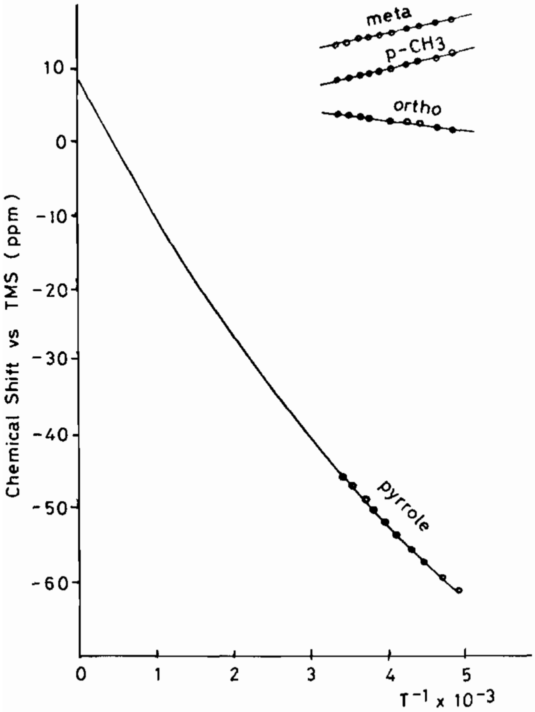

Fig. 4. Curie plot for the Ru(IV)(TpTP)Br_2 resonances.

It is concluded that this is positive spin density at the *meso* carbon as phenyl resonances follow the pattern of the cation radical discussed above. It is consistent with delocalization of unpaired spin density from the d_{xz}, d_{yz} orbitals to the empty 4e(π*) orbitals (M → L charge transfer).

In the course of the process studied, the monobromo pyrrole substituted derivatives were formed and traced in NMR spectra. Seven widely spread pyrrole resonances flanked the pyrrole one of Ru(IV)TTPBr_2 (−37.32; −39.45; −42.04; −42.09; −52.00; −53.29; −54.89 ppm in $CDCl_3$ at 25 °C, Fig. 1c). Their positions reflect the asymmetry of spin distribution due to the symmetry lowering. Further experiments aiming to generate Ru(IV) porphyrin systems are in progress.

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