Determination of Rh–C Bond Dissociation Energy in Methyl(porphyrinato)rhodium(III) Complexes: a New Application of Photoacoustic Calorimetry

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The photolysis of $RhCH_3$(ttp) and $RhCH_3$(tmp) (ttp = 5,10,15,20-tetratolylporphyrin, tmp = 5,10,15,20-tetramesitylporphyrin) was studied in methanol at ambient temperature: the quantum yields for photolysis were determined to be 0.51 and 0.54, respectively, and the Rh–C bond dissociation energies (227 and 219 kJ mol^{-1}, respectively) were measured by photoacoustic calorimetry, which were larger than those of Co–C bond.

Rhodium porphyrins, which could act as models for reactive species in catalytic and photochemical reactions, have provided a variety of new examples of unusual reactivity in organometallic chemistry.[1,2] It has been reported that the non-bridged metal–metal dimers and sterically hindered monomers present special chemical reactivities in C–H activation and olefins insertion.[1b–1d] Furthermore, alkyl 1,2-rearrangements of rhodium porphyrins have been studied due to their potential relevance to the coenzyme B_{12} dependent enzymatic reactions.[2] In order to gain insight into the nature of the mechanism and the reactivity of organorhodium complexes related reactions, a knowledge of both kinetics and thermodynamics of such processes is highly desirable. However, there is few rhodium–carbon bond dissociation energies (BDE) reported in the literature.[3–5] Since Rh–C bonds are expected to be stronger than Co–C bonds,[4] it is obviously difficult to make such measurements by conventional thermal kinetic methods. During the past decades, photoacoustic calorimetry (PAC) has been used to determine the energetics and kinetics for photoinduced reactions.[6–8] Some metal–ligand bond dissociation energies were measured by this approach.[6d,8] In this paper we reported the Rh–C bond dissociation energies of $RhCH_3$(ttp) **1** and $RhCH_3$(tmp) **2** by using photoacoustic calorimetry.

$$\mathrm{Rh^{III}CH_3(por)} \xrightarrow{h\nu} [\,\mathrm{Rh^{III}CH_3{:}(por)}] \longrightarrow \mathrm{Rh^{II}(por)} + \mathrm{CH_3^{\bullet}} \qquad (1)$$

por = ttp **1**, tmp **2**

The principles of the photoacoustics have been well established. Our experimental setup is similar to those previously described.[9] When **1** and **2** are irradiated (λ = 355 nm) in methanol under argon atmosphere at room temperature, Rh–C bond undergoes cleavage to form Rh^{II}(por) and methyl radical cage pair, and then the caged pair will diffuse into the solvent rapidly (eq 1).[10] Since the concentrations of the photolytic products of **1** and **2** should be less than 10^{-6} M for the sample concentrations of about 10^{-5} M, the subsequent diffusive recombination and radical reactions could be neglected. Therefore, when the PAC experiment is performed under these conditions using a 1.5-MHz transducer, which has time windows of 100 ns, Rh^{II}(por) and methyl radical are the final products, and the enthalpy change due to the cleavage of such specific bond could be examined.[11] From a plot of the photoacoustic signal amplitude in methanol under argon versus relative laser intensity, the ratio of the slope of the sample to that of ferrocene yields α, the fraction of the photon energy converted into prompt heat. The observed heat deposition is related to the term α by eq 2,

$$\Delta H_R = E_{h\nu}(1-\alpha)/\Phi \qquad (2)$$

where $E_{h\nu}$ is the photon energy (336 kJ mol^{-1} at 355 nm) and Φ is the quantum yield for photodissociation. The quantum yields for the photolysis of **1** and **2** are measured in methanol with excess TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy) under argon.[12] In our case the heat accompanying Rh–C bond homolysis in methanol has been measured, and the overall enthalpy change of the reaction may correspond to such bond dissociation energy.[13] The results for **1** and **2** are summarized in Table 1.

Table 1. Rh–C bond dissociation energies determined by photoacoustic calorimetry

Compound	α	Φ	BDE /kJ mol^{-1}
1	0.656±0.005	0.51±0.03	227±13
2	0.648±0.005	0.54±0.03	219±10

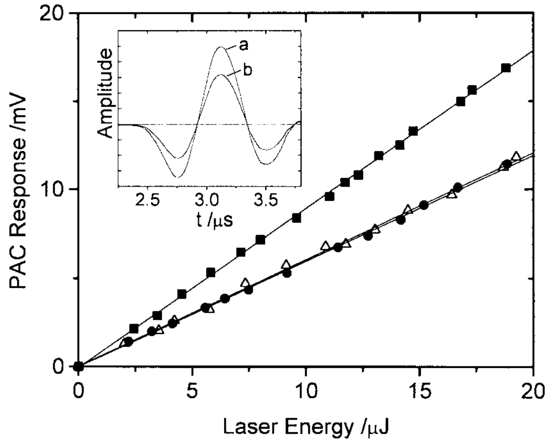

Figure 1. Photoacoustic response for the photodissociation of $RhCH_3$(ttp) (•) and $RhCH_3$(tmp) (Δ) in methanol. The response for ferrocene (■) is shown for comparison. Inset shows the normalized photoacoustic signals of (a) ferrocene and (b) $RhCH_3$(tmp) in methanol under argon atmosphere.

It is noted that the Rh–C BDE values of **1** and **2** determined by PAC are in agreement with the estimated bond energy for Rh–CH_3 (~242 kJ mol^{-1}).[14] As can be seen from the results in Table 1, the Rh–C BDE value of **1** is comparable to that of **2**. Most likely, the similarity in equatorial porphyrin ligand should not introduce a big difference in Rh–C BDE.

By comparison of Rh–C BDEs in **1** and **2** with those of organo Rh(OEP) complexes,[15] the Rh–C bond strength follows the order Rh(OEP)CH(Bu)OH < **1, 2** < Rh(OEP)CHO. The reasonable explanation is that the dissociation of the Rh–C bond involves reduction of organorhodium(III) complex to Rh(II) product. Thus, more electron-withdrawing ligands (CHO > CH_3 > CH(Bu)OH) are expected to stabilize the Rh(III) complexes, and hence, to increase energy for such bond cleavage.[16,17] Unfortunately, the existing literature values for Rh–C BDE are sparse and uncertain, so it is difficult to make further comparisons.

It is well recognized that the bond dissociation energies for Rh–C bond (167–250 kJ mol^{-1}) are higher than those for Co–C bond (84–125 kJ mol^{-1}) in corresponding organometallic complexes. The greater stability of Rh–C bond could be attributed to improved bonding overlap of 4d orbitals of rhodium atom and alkyl orbital. It is suggested that unfavorable steric interaction is probably predominant to the Co–C bond because the smaller radial distribution of the 3d valence orbitals compared to the 4d requires a shorter M–C bond length to maximize the bonding overlap.[4] The light stability[10] of our organorhodium complexes is presumably dependent on the high Rh–C BDE, the lifetime of photoactive state and the efficiency of the recombination. However, these mechanisms require more detail investigation.

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9 A laser pulse from Q-switched Nd:YAG laser (Continuum NP70) operated at 355 nm, 10 Hz, and 8-ns duration was passed through the sample solution held in a 1-cm thermostated flow cell. The acoustic wave induced in solution was detected by a 1.5-MHz PZT piezoelectric transducer. The signal was then pre-amplified by a HP-8847F and recorded by a 300-MHz HP-54510B digital oscilloscope as the average of 100 laser shots. The data were stored in a PC for analysis. Ferrocene, a calorimetric reference, was sublimed once before use. For each photoacoustic experiment, it was dissolved in the same medium and matched in OD at 355 nm to those of **1** and **2**.

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11 The signal frequency for sample is identical to that of the calorimetric reference, ferrocene, which relaxes back to ground state within 1ns. Thus, no heat releases on the time-scale of about 10 ns to 10 µs.

12 a) Samples were photolyzed at 355 nm, in the presence of TEMPO, to ca. 5% conversion, and the products were analyzed by UV–vis spectrometer. The quantum yield for photolysis of **1** and **2** could be measured according to the equation,

$$\Phi_s = \frac{(\Delta A_s / E_a)\varepsilon_2^r}{(\Delta A_r / E_a)(\varepsilon_1^s - \varepsilon_2^s)}\Phi_r ,$$

where Φ_s and Φ_r are the quantum yields for the photolysis of sample and actinometer, $\Delta A_s/E_a$ and $\Delta A_r/E_a$ are the energy normalized absorbance changes for sample and actinometer, ε_1^s and ε_2^s are the extinction coefficients of the sample and its photolytic product, and ε_2^r is the extinction coefficient of the actinometer. Potassium ferrioxalate actinometer was used as described in ref 12b. In the quantum yield calculations, the corrections are made for absorption of TEMPO and Rh(II) species. b) J. G. Calvert and J. N. Pitts, Jr. “Photochemistry,” John Wiley & Sons, Inc., New York (1966), p. 783.

13 Since **1** and **2** are rigid complexes, the reaction volume changes during their photolysis are so small that they could be neglected, especially in organic solvent.

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15 The Rh–C BDE for Rh(OEP)CHO is 242 kJ mol^{-1}, and that for Rh(OEP)CH(Bu)OH is 118 kJ mol^{-1}. See ref 3 and references herein.

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