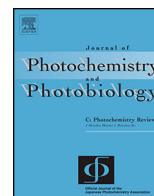




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Review

Primary reactions in the photochemistry of hexahalide complexes of platinum group metals: A minireview



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ABSTRACT

We review the results obtained for $\text{Pt}^{\text{IV}}\text{Cl}_6^{2-}$, $\text{Pt}^{\text{IV}}\text{Br}_6^{2-}$, $\text{Ir}^{\text{IV}}\text{Cl}_6^{2-}$, $\text{Ir}^{\text{IV}}\text{Br}_6^{2-}$, and $\text{Os}^{\text{IV}}\text{Br}_6^{2-}$ complexes in aqueous and alcoholic solutions using ultrafast pump–probe spectroscopy, laser flash photolysis, ESR, and photoelectron spectroscopy. We discuss the correlations between the photophysics and the photochemistry of these complexes. The key reaction for $\text{Pt}^{\text{IV}}\text{Cl}_6^{2-}$ is the inner-sphere electron transfer, which results in an Adamson radical pair that lives for several picoseconds, and the subsequent photoaquation in aqueous solutions and photoreduction in alcohols. The chlorine atom formed as the primary product escapes the solvent cage in aqueous solutions or oxidizes a solvent alcohol molecule via secondary electron transfer, producing secondary intermediates that react on the microsecond time scale. The photoexcitation of $\text{Pt}^{\text{IV}}\text{Br}_6^{2-}$ results in the formation of pentacoordinated Pt^{IV} intermediates, i.e. $^3\text{Pt}^{\text{IV}}\text{Br}_5^-$ and $^1\text{Pt}^{\text{IV}}\text{Br}_5^-$, with characteristic lifetimes of approximately 1 and 10 ps, respectively. Subsequent reactions of these intermediates result in the complexation of a solvent molecule. Photoreduction is also possible in alcohols. Similar reactions occur with rather low quantum yields for $\text{Ir}^{\text{IV}}\text{Cl}_6^{2-}$, therefore, only the ground-state recovery could be monitored in ultrafast experiments, which occur on the 10-ps time scale. The photochemical behaviours of the $\text{Ir}^{\text{IV}}\text{Br}_6^{2-}$ and $\text{Os}^{\text{IV}}\text{Br}_6^{2-}$ complexes are similar to those of $\text{Ir}^{\text{IV}}\text{Cl}_6^{2-}$ and $\text{Pt}^{\text{IV}}\text{Br}_6^{2-}$, respectively.

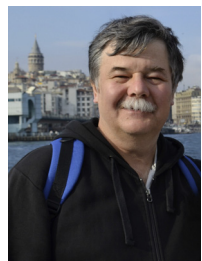
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include education and climate-related issues: <http://goo.gl/7yvA7>.

1. Introduction

The photochemical activity of platinum group metal complexes was discovered almost 200 years ago [1]. The photochemistry of hexahalide complexes of platinum group metals ($M^{IV}X_6^{2-}$) was

considered to be a subject of solely academic relevance until the end of the 20th century [2–5]. The principal focus has been on the $Pt^{IV}Cl_6^{2-}$ complex. The main points investigated were the reaction intermediates [6–12], unusual aquation chain reactions [11,12] and the dramatic differences in the properties of the isoelectronic $Pt^{IV}Cl_6^{2-}$ and $Pt^{IV}Br_6^{2-}$ complexes [2,3].

Currently, the practical needs of various technological applications provided new stimuli for photochemical studies of these complexes. The best-known application is in photocatalysis. The four-electron photoreduction of Pt^{IV} to Pt^0 in water–alcohol mixtures discovered by Cameron and Bocarsly [13,14] initiated the use of $Pt^{IV}Cl_6^{2-}$ photolysis to produce platinum nanoparticles [15–22]. Generally, the direct photoreduction of metal cations has been established as an important method to produce nanoparticles that are free from chemical reducing agents (see [15] and references therein).

One of the fundamental problem in photocatalysis is extending the absorption spectra of cheap semiconductors (TiO_2 , CdS) into the visible spectral range. One excellent approach is modifying TiO_2 [23–27] or CdS [28–30] surfaces with metallic platinum via the photoreduction of hexachloroplatinate. The photochemical modification of the TiO_2 surface by iridium was also reported [31]. Proper descriptions of such systems require knowledge about both the heterogeneous chemistry and photochemistry of the complexes formed by the desorbed metal atoms in solution [24].

Photodynamic therapy (PDT) is another important application of these complexes, joining the high cytotoxicity of platinum group metals to other advantages of PDT, i.e. the selectivity and the low systemic toxicity [32,33]. Typically, platinum complexes are used in PDT, see [32–35] and the references therein. Additionally, the photolysis products of ammonium hexachloroiridate(IV) have been reported to have anti-tumour and antimutagenic activities by Gale et al. [36]. Organoiridium [37] and cyclometallated iridium complexes [33,38,39] were also proposed as prospective anticancer agents.

An interesting application of hexachloroiridates was proposed by Gupta et al. [40,41]. They offered a combined photoelectrochemical method of hydrogen and chlorine production from hydrochloric acid that is assisted by a mixture of $Ir^{IV}Cl_6^{2-}$ and $Ir^{III}Cl_6^{3-}$ complexes as a photocatalyst.

Successful application of photochemical reactions requires detailed knowledge of the reaction mechanism. A straightforward way to obtain such knowledge is to follow the entire reaction path from the ultrafast primary processes to the final products. In practice, the reaction mechanisms in the photochemistry of coordination compounds were usually proposed based on the results of steady-state experiments because the ability to follow the primary reactions was lacking [2–5]. Often, the involvement of short-living reactive intermediates, such as Adamson's radical pairs [42], has been merely postulated without any direct evidence. Currently, these mechanisms may be examined via advanced time-resolved methods, starting at the femtosecond time resolution.

The study of the ultrafast dynamics of transition metal complexes is an active area of research in chemical physics [43–51]. Nevertheless, primary photophysical processes are known in detail for only a few types of transition metal complexes. These include Cr(III) complexes [46–48], polypyridyl complexes of Ru(II) [43,44,52], and metal carbonyls [43,51]. Additionally, complexes demonstrating spin crossover are being actively studied [50,53].

Presently, we review the experimental work on the primary photophysical and photochemical reactions of $M^{IV}X_6^{2-}$ complexes via ultrafast kinetic spectroscopy.

2. Experimental setups, kinetic curves and data treatment

The experiments in the ultrafast kinetic spectroscopy of the $Pt^{IV}Cl_6^{2-}$, $Pt^{IV}Br_6^{2-}$ and $Ir^{IV}Cl_6^{2-}$ complexes were performed using

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