PHOTOREDUCTION OF CERIUM(IV) HEXACHLORIDE IN ACETONITRILE

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Summary

Irradiation of $CeCl_6^{2-}$ in acetonitrile solution resulted in photoreduction to cerium(III) with constant quantum yields at all wavelengths corresponding to the charge transfer bands. The process occurred by direct electronic transfer from the ligand to the metal, the subsequent release of the oxidized ligand and rearrangement with the uptake of another ionic ligand, if present, or of solvent molecules. The dependence of the quantum yield on the substrate concentration, the light intensity and the irradiation time was attributed to quenching by the cerium(III) photoproduct.

1. Introduction

The investigation of photoredox reactions in transition element compounds is a useful method of obtaining information about the nature of the electronic transitions and the reactivity of the related excited states. The results are more significant when the irradiation is carried out at wavelengths corresponding to bands in the absorption spectrum and when the compounds are irradiated in aprotic solutions which minimize probable secondary reactions.

Our earlier investigations of uranium(IV), UO_2^{2+} and cobalt(III) compounds [1, 2] emphasized the close relation between the photoreaction and the excited band as the redox processes occurred only from charge transfer states which had been populated directly by suitable irradiation. In the present paper we report the photochemical behaviour of tetra(ethyl)ammoniumhexachloridecerium(IV) ($[(C_2H_5)_4N]_2CeCl_6$) in acetonitrile solution. Previous investigations of cerium complexes [3 - 5] have been carried out in aqueous media and in protic solvents, and the photoreactions observed under such conditions involved solvent participation.

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2. Experimental details

$[(C_2H_5)_4N]_2CeCl_6$ was prepared by mixing cold solutions of $Ce(SO_4)_2$ and $(C_2H_5)_4NCl$ in concentrated HCl. The $[(C_2H_5)_4N]_2CeCl_6$ precipitate was washed first with cold concentrated HCl and then with acetone and was finally dried.

$[(C_2H_5)_4N]_3CeCl_6$ was obtained in solution by dissolving $CeCl_3 \cdot xH_2O$ in acetonitrile containing excess $(C_2H_5)_4NCl$ [6]. Standard irradiation equipment was used. The irradiation at 254 nm was performed using a low pressure mercury vapour lamp (Hanau NN 15/44). The radiation at 333 and 365 nm was obtained from a mercury vapour lamp (Hanau Q 400) using interference filters (Schott Gen.). The intensity of the incident light was measured using a ferric oxalate actinometer and was of the order of 10^{-7} - 10^{-6} einstein min^{-1}.

The samples to be irradiated were sealed in spectrophotometric cells after nitrogen had been bubbled through them for a long time. The reaction kinetics were followed spectrophotometrically in the appropriate absorption region. The spectrophotometric measurements were performed using an Optica CF4Ni spectrophotometer with the temperature of the cell compartment kept constant at 25 °C.

Benzyl chloride was identified gas chromatographically using the following technique. 6 ml of water was added to 6 ml of the reaction mixture. The organic layer was dried over Na_2SO_4 and was then injected directly into a gas–liquid chromatography column. Benzyl chloride was identified by comparison with a standard sample injected at the same time. The gas chromatographic separation was effected using a silanized glass column of dimensions 2 m × 4 mm containing 5% QF-1 on Chromosorb W (80 - 100 mesh; washed with acid and treated with dimethylchlorosilane) at 100 °C. Nitrogen was used as the carrier gas (flow rate, 30 ml min^{-1}).

3. Results and discussion

The spectrum of $[(C_2H_5)_4N]_2CeCl_6$ shows two intense bands at 375 nm (ϵ = 5200) and at 255 nm (ϵ = 13 500) which were assigned by Ryan and Jorgensen [6] to electron transfer from the highest filled molecular orbital, which is mainly localized on the halide ligands, to the empty 4f orbitals. The spectrum of $[(C_2H_5)_4N]_3CeCl_6$ consists of a single strong band at 330 nm (ϵ = 1600) which was ascribed [6] to the electron transition $4f \rightarrow 5d$.

When deaerated acetonitrile solutions of $CeCl_6^{2-}$ are irradiated at 254, 333 and 365 nm, the cerium(IV) undergoes photoreduction to cerium(III) at all exciting wavelengths. On irradiation of solutions containing excess $(C_2H_5)_4NCl$ the spectrum of the irradiated sample fits that of a mixture of $CeCl_6^{2-}$ and $CeCl_6^{3-}$ with a total concentration exactly equal to the initial concentration of $CeCl_6^{2-}$ (Fig. 1). On irradiation of solutions which do not contain $(C_2H_5)_4NCl$ chlorosolvated cerium(III) species that were converted

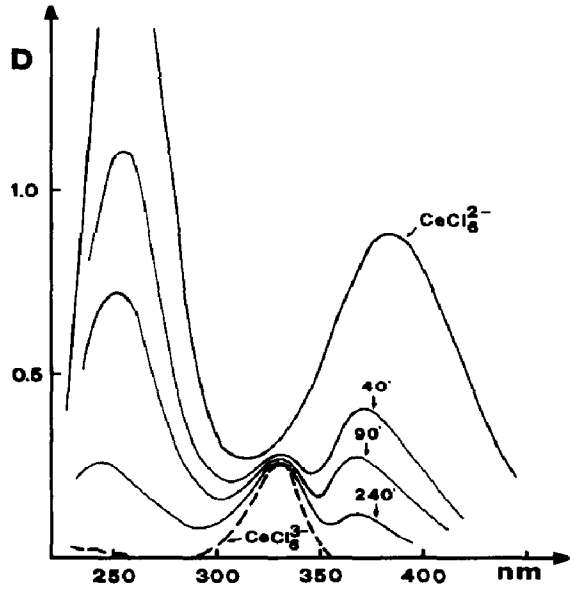

Fig. 1. Changes in the absorption spectra of $CeCl_6^{2-}$ in acetonitrile obtained at various irradiation times in the presence of excess $(C_2H_5)_4NCl$ (λ_{irr} = 254 nm).

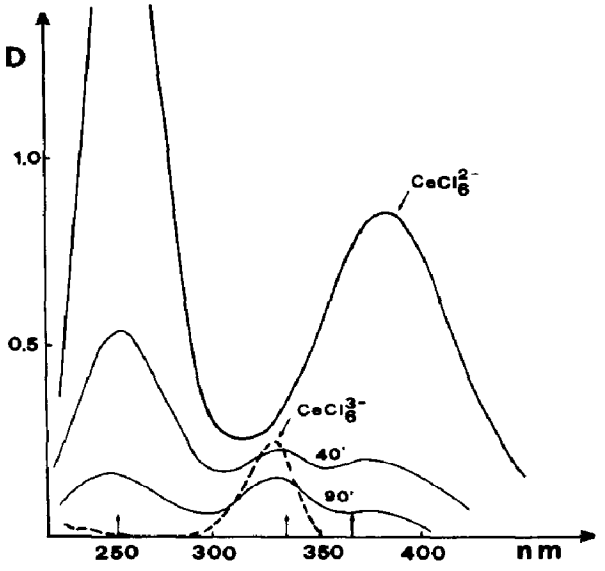

Fig. 2. Changes in the absorption spectra of $CeCl_6^{2-}$ in acetonitrile obtained at various irradiation times in the absence of $(C_2H_5)_4NCl$ (λ_{irr} = 254 nm): – – –, spectrum of the photolysed solution after the addition of excess $(C_2H_5)_4NCl$.

quantitatively to $CeCl_6^{3-}$ by the subsequent addition of $(C_2H_5)_4NCl$ (Fig. 2) were obtained. Therefore the photoreduction of cerium(IV) to cerium(III) occurs without side reactions and can be described as a process involving the homolytic cleavage of the Ce—Cl bond and the formation of the chloro radical according to the following scheme:

$$[CeCl_6]^{2-} \xrightarrow{h\nu} [CeCl_5]^{2-} + Cl^{\cdot} \quad (1)$$

$$[CeCl_5]^{2-} + Cl^{-} \rightarrow [CeCl_6]^{3-} \quad (2)$$

$$[CeCl_5]^{2-} \xrightarrow{NCCH_3} [CeCl_{6-n}(NCCH_3)_n]^{(3-n)-} + (n-1)Cl^{-} \quad (3)$$

$$Cl^{\cdot} + Cl^{-} \rightleftharpoons Cl_2^{\cdot -} \quad (4)$$

In the presence of $(C_2H_5)_4NCl$ fast complexation of the photoformed cerium(III) species occurs (reaction (2)), while in the absence of the free ligand rapid solvation reactions of cerium(III) take place leading to the probable formation of complexes of the type $[CeCl_{6-n}(NCCH_3)_n]^{(3-n)-}$ (reaction (3)) in mutual equilibrium. However, the band appearing at 330 nm shows that under these conditions part of the cerium(III) is in the form $CeCl_6^{3-}$. We proved that chloro radicals had been formed by making use of their well-known ability to promote chlorination reactions in the organic substrate [7]. Toluene was employed as a radical scavenger. Solutions of $CeCl_6^{2-}$ in acetonitrile, which does not react easily with the chloro radical [8], to which 20 vol.% toluene had been added were irradiated until complete conversion to $CeCl_6^{2-}$ had taken place. A subsequent gas chromatographic analysis showed that benzyl chloride was present in these solutions, thus proving that chloro radicals had been formed during the irradiation.

Our experimental results did not allow us to determine whether the released ligand was in the form of the chlorine radical $Cl^{\cdot}$ or the anion radical $Cl_2^{\cdot -}$. However, the association of the chlorine radical and the chloride ion with the formation of an anion radical $Cl_2^{\cdot -}$ has been observed in flash photolysis and pulse radiolysis investigations of aqueous and acetonitrile solutions of alkali halides and halogenated complexes [8 - 14]. Since the conditions of our experiments were analogous to those in which $Cl_2^{\cdot -}$ formation has been demonstrated, it is reasonable to assume that the anion radical $Cl_2^{\cdot -}$ was formed during the photolysis of $CeCl_6^{2-}$.

The kinetics of the photochemical reaction were studied under various experimental conditions in order to determine the factors influencing the reaction. It was found that complete conversion of cerium(IV) to cerium(III) with constant quantum yield ($\Phi = 0.065 \pm 0.002$) independent of the irradiating wavelength was obtained only in experiments carried out using solutions of low substrate concentration (2×10^{-4} M or less) and low light intensities. Under these conditions the photochemical process is not perturbed by quenching reactions; moreover the $Cl_2^{\cdot -}$ radical is destroyed by secondary processes such as solvent quenching or self-quenching that we were unable to identify.

Under different experimental conditions some thermal reactions, which alter the observed kinetics, occur subsequent to the pure photochemical process. In fact increases in the substrate concentration, the light intensity and the $(C_2H_5)_4NCl$ concentration act synergically to decrease the photoreduc-

TABLE 1

Dependence of the initial quantum yield on the $CeCl_6^{2-}$ and $(C_2H_5)_4NCl$ concentrations

Φ	$[CeCl_6^{2-}]$ ($\times 10^{-3}$ M)	$[Cl^-]$ ($\times 10^{-2}$ M)
0.064	0.1	—
0.035 [a]	0.2	—
0.066	0.2	—
0.050	0.2	0.2
0.044	0.2	0.8
0.040	0.2	2.0
0.044	0.4	0.2
0.040	0.6	0.2
0.037	0.8	0.2
0.034	1.0	0.2

λ_{irr} = 365 nm; light intensity, 3×10^{-7} einstein min^{-1}.
[a]Light intensity, 7.5×10^{-7} einstein min^{-1}.

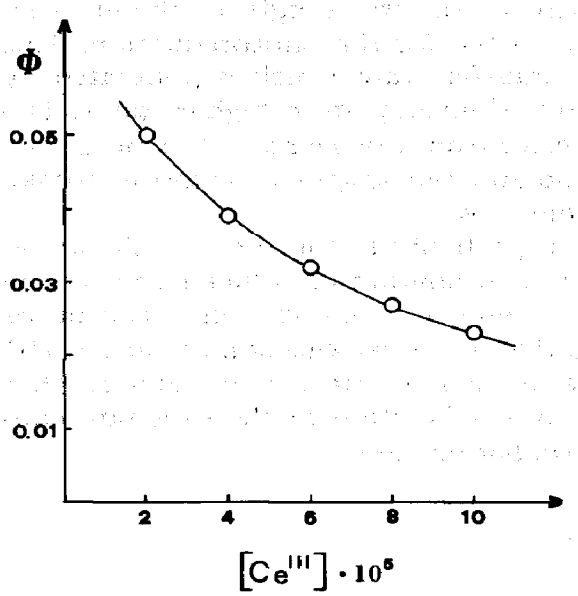

Fig. 3. Quantum yield calculated at various times after irradiation as a function of the concentration of photoformed cerium(III): $[CeCl_6^{2-}] = 0.2 \times 10^{-3}$ M; $[Cl^-] = 2 \times 10^{-3}$ M; λ_{irr} = 365 nm.

tion quantum yield (Table 1) which becomes dependent on the irradiation time (Fig. 3); under these conditions a pseudoequilibrium state can be observed.

The observed decrease in the quantum yield can be attributed to quenching of the $Cl_2^{\bullet -}$ by the cerium(III) in a back reaction to cerium(IV) when the concentrations of the two species are at an appropriate level for such a reaction to occur; both a high substrate concentration and a strong

light intensity provide high local concentrations of $Cl_2^{\cdot -}$ and cerium(III). The variation in the quantum yield with the irradiation time is further evidence for the importance of the reoxidation of cerium(III) by the radicals generated during the irradiation.

Two experiments demonstrate the correctness of this interpretation. First the addition of a very concentrated solution of $CeCl_6^{3-}$ quenched the photoreduction. Secondly a comparison of the results obtained on irradiating two solutions of the same concentration ($[CeCl_6^{2-}] = 10^{-3}$ M and $[Cl^-] = 2 \times 10^{-2}$ M) at the same light intensity (3×10^{-7} einstein min^{-1}), only one of which contained the toluene scavenger, showed that when toluene was present the reaction proceeded until the reduction of $CeCl_6^{2-}$ to $CeCl_6^{3-}$ was complete, whereas in its absence the reaction stopped at a transformation of less than 50%.

The variation in the quantum yield with the $(C_2H_5)_4NCl$ concentration indicates that a decrease in the Cl^- concentration favours the disappearance of the $Cl_2^{\cdot -}$ via alternative cerium(III) oxidation pathways [14].

In conclusion, the excitation of $CeCl_6^{2-}$ in charge transfer bands promoted the photoreduction of cerium(IV) to cerium(III). The observation that the quantum yield was independent of the wavelength of the exciting light suggests that a single state is responsible for the photoreduction. This state could be the lower-lying charge transfer state which is populated by direct excitation or by decay with unit efficiency from higher states. The process occurs by direct electronic transfer from the ligand to the metal, the subsequent release of the oxidized ligand and rearrangement with the uptake of another ionic ligand or of solvent molecules.

The release of the oxidized ligand, probably in the form of the anion radical $Cl_2^{\cdot -}$, was demonstrated by the chlorination of toluene and by the quenching of the photoreaction in the presence of a high concentration of $CeCl_6^{3-}$ which was interpreted as being due to the reoxidation of cerium(III) by $Cl_2^{\cdot -}$. It is precisely because of the quenching effect of cerium(III) that the quantum yield of the photoreaction is a function of the substrate concentration, the light intensity and the irradiation time.

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