Optical Outer-Sphere Charge Transfer in Ion Pairs with Peroxoborate as Donor

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Peroxoborate and the oxidizing cations [Co(NH₃)₆]Cl₃, [Ru(NH₃)₆]Cl₂ and N,N'-dimethyl-4,4'-bipyridinium²⁺ (parquat⁺) form ion pairs in aqueous solutions which display outer-sphere charge transfer (OSCT) bands in their absorption spectra. This CT involves an electronic transition from the peroxy substituents of peroxoborate to the cations. When 10,10'-dimethyl-9,9'-biaclidinium²⁺ (lucigenin⁺, LG⁺) is used as an electron acceptor an OSCT absorption is not observed owing to the instability of the ion pair LG⁺ peroxyborate which undergoes a chemiluminescent conversion to N-methylacridone.

1. Introduction

Hydrogen peroxide is a reductant as well as an oxidant. Accordingly, it tends to dismutate to water and oxygen. This ambivalence is also documented by the electronic spectra and photochemistry of transition metal complexes with peroxide as ligand. In combination with reducing and oxidizing metals low-energy metal-to-ligand charge transfer (MLCT) [1, 2] and ligand-to-metal charge transfer (LMCT) [3, 4] transitions occur, respectively. While MLCT excitation leads to the reduction of peroxide to water, LMCT transitions induce the oxidation of peroxide to oxygen. The application of O₂⁻ as a CT donor or acceptor could be considerably extended if it would participate in optical outer-sphere charge transfer (OSCT). It is well known that ion pairs which consist of oxidizing cations and reducing anions display OSCT bands in their electronic spectra [5, 6]. It follows that ion pairs of oxidizing cations and peroxide should display OSCT absorptions. Unfortunately, peroxide is a strong base and nucleophile. It is thus hardly suitable as counter ion in ion pairs. However, these detrimental properties can be avoided if peroxide is incorporated in other possibilities. We explored this possibility and selected peroxyborate (or perborate) as donor for the present study. It is available as NaBO₃·H₂O. The complex cations [Ru(NH₃)₆]³⁺ and [Co(NH₃)₆]³⁺ as well as the organic cations N,N'-dimethyl-4,4'-bipyridinium²⁺ (parquat²⁺, PQ²⁺) and 10,10'-di-

2. Results

The compounds NaBO₃·H₂O, [Ru(NH₃)₆]Cl₃, [Co(NH₃)₆]Cl₃, PQCl₂ and LG(NO₃)₂ are commercially available (Aldrich). Aqueous solutions of PQCl₂ or NaBO₃·H₂O are colourless and do not absorb above 330 nm. Upon mixing aqueous PQ²⁺ and BO₃⁻ the combined solutions immediately turn yellow. This colour is caused by a new absorption (Fig. 1) at λ_max = 388 nm. At fairly high equimolar concentrations (> 7 x 10⁻³ M) of both ions this band follows the Lambert-Beer law with ε = 6 dm³ M⁻¹ cm⁻¹. It is assumed that at this concentration ion pairing is complete. The deviation

Fig. 1. Electronic absorption spectra of aqueous 1.8 x 10⁻² M PQCl₂ (a) and an equimolar (1.8 x 10⁻² M) mixture of PQCl₂ and NaBO₃·H₂O (b) in water at room temperature, 1-cm cell.

methyl-9,9'-biaclidinium²⁺ (lucigenin, LG²⁺) were chosen as electron acceptors [5, 6].
from the Lambert-Beer law at much lower concentrations (< 10^{-3} M) is used to estimate the ion pair association constant. The ion pair PQ2^{+}BO_{3}^{-} is of moderate stability (K = 220 M^{-1}).

Similar observations are made when colourless solutions of [Ru(NH_{3})_{6}]Cl_{3} and NaBO_{3}×H_{2}O are mixed. Again, this mixture turns yellow owing to a new absorption (Fig. 2) at \(\lambda_{\text{max}} = 402\) nm. Further measurements were hampered by a precipitate which is formed at higher concentrations (> 5 × 10^{-3} M), but the extinction coefficient of the 402 nm absorption was estimated to be \(\varepsilon \sim 4\).

Upon mixing aqueous [Co(NH_{3})_{6}]Cl_{3} and NaBO_{3}×H_{2}O a precipitate is formed. Only at rather low concentrations (< 1 × 10^{-3} M) a homogeneous solution is obtained. The appearance of a new absorption at \(\lambda_{\text{max}} = 283\) nm which is attributed to the ion pair [Co(NH_{3})_{6}]^{2+}BO_{3}^{-} is derived from the difference spectrum.

When aqueous solutions of LG(NO_{3})_{2} and NaBO_{3}×H_{2}O are mixed a thermal reaction takes place which is accompanied by a chemiluminescence (Fig. 3). LG^{2+} is well known to show this chemiluminescence when it reacts with H_{2}O_{2} in alkaline solution [7].

3. Discussion

A variety of ion pairs which consist of oxidizing cations and reducing anions display long-wavelength OSCT absorptions [5, 6]. Owing to its general importance the peroxide anion would be a CT donor of particular interest. Reductions by peroxide could then be also performed as photochemical reactions induced by OSCT excitation. As final oxidation product molecular oxygen should be formed. Unfortunately, O_{2}^{2-} exists only in strongly alkaline solution. It is easily protonated in protic solvents but reacts also thermally with many electron-poor compounds. The nucleophilicity of O_{2}^{2-} can be prevented if it is covalently attached to other atoms. We found that NaBO_{3}×H_{2}O is suitable for our purpose. Various alkali peroxoborates of the general composition MBO_{3}×nH_{2}O contain the peroxo-bridged anion [B_{2}(O_{2})(OH)_{4}]^{2-} in the solid state [8 - 11]. In aqueous solution other anions with boron-peroxo moieties are also present [12 - 14]. This complication certainly interferes with a quantitative assessment. Accordingly, the extinction coefficients and stability constants of the ion pairs should be considered with caution. As an operational definition these various peroxoborates which are formed in solution are called BO_{3}^{-} in this paper.

The aqueous ion pairs of BO_{3}^{-} and the oxidizing cations [Co(NH_{3})_{6}]^{3+}, PQ^{2+} and [Ru(NH_{3})_{6}]^{3+} show OSCT transitions at \(\tilde{v}_{\text{max}} = 35340, 25770\) and 24880 cm^{-1}, respectively. This red shift qualitatively correlates with an increase of the oxidizing strengths of the cations (E_{e}): [Co(NH_{3})_{6}]^{3+}, -0.76 V < PQ^{2+}, -0.42 V < [Ru(NH_{3})_{6}]^{3+}, +0.05 V [15, 16], [Co(NH_{3})_{6}]^{3+} is reduced at E_{e} = +0.06 V. This potential is associated with the formation of the high-spin ground state of [Co(NH_{3})_{6}]^{2+}, but it is lower by 0.82 V for the low-spin form which is generated in optical OSCT transitions [16]. However, a quantitative correlation between OSCT energies and redox
potentials is missing, but this not surprising. Deviations are certainly caused by different reorganization energies which are associated with the reduction of the cations [17]. In the case of [Co(NH₃)₆]³⁺ this contribution is rather large since the electron is accepted by a σ antibonding eg orbital [18]. This is in contrast to [Ru(NH₃)₆]³⁺ which is not expected to undergo large structural rearrangements because the reduction involves the population of a non-bonding t₂g orbital.

Lucigenin is also able to function as an OSCT acceptor [19]. However, the ion pair LG²⁺BO₃⁻ is not stable but reacts thermally. As indicated by the concomitant occurrence of a chemiluminescence this reaction is attributed to the depicted process.

This chemiluminescence proceeds apparently in analogy to related reactions of lucigenin with other peroxide sources [7, 20].

In summary, it has been shown that peroxoborate is a versatile CT donor for oxidizing cations. It is anticipated that peroxoborate or other peroxide-containing anions will be useful photoreductants in future applications.

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