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Chemiluminescence Spectroscopic Identification of Copper(III) in High-temperature Superconductors *via* Reaction with $[Ru(bpy)_3]^{2+}$ in Solution (bpy = 2,2′-bipyridyl)

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A new method has been found for the identification of copper(III) in high-temperature superconductors, based on recording the light emitted on interaction of the superconductors with tris(2,2′-bipyridyl)ruthenium(II) chloride in solution.

The determination of the degree of oxidation of copper in 1-2-3 ceramics is an important problem both in the analysis of high-temperature superconductors (HTSC) and as regards our understanding of the mechanism of superconductivity. An analysis of literature data by Grazhulene and Karpov[1] showed that copper can exist in superconductors in the form of Cu^{III} and Cu^{II}. The most important properties of superconductors depend significantly on the ratio of the heterovalent forms of copper. We found that the presence of Cu^{III} in HTSC can be established unambiguously from the chemiluminescence observed on dissolution of HTSC specimens in aqueous acid solutions of the divalent ruthenium complex $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (bpy = 2,2′-bipyridyl).†

Chemiluminescence was also observed on dissolution of HTSC in aqueous HCl and H_2SO_4 solutions not containing the ruthenium complex. Its intensity is weaker by more than two orders of magnitude, which precludes the measurement of the spectrum of this background chemiluminescence. A light-limiting filter KS-II (which has a 50% transmittance at 613 nm) attenuates the background chemiluminescence by only 50%. This means that a large proportion of the background chemiluminescence is concentrated in the red and IR regions of the spectrum. The absence of photoluminescence from the solution after the dissolution of the HTSC in acids indicates the unstable nature of the emitter of this chemiluminescence. We suggest that excited singlet oxygen ($^1O_2$) is a chemiluminescence emitter of this kind. On energy grounds, its generation may be accomplished by the oxidation of water by trivalent copper ($-H = 3.03$ eV), *i.e.* reaction (4).

The chemiluminescence spectrum recorded on dissolution of the HTSC in Ru^{II} solutions is located in the range 520–700 nm with a maximum at 600 nm. It is satisfactorily correlated with the photoluminescence spectrum of the initial ruthenium(II) complex. The total light emitted in these experiments varies linearly with the Ru^{II} concentration in solution in the range 10^{-4}–10^{-3} mol dm^{-3}. Thus, $\{[Ru(bpy)_3]^{2+}\}^*$ is the chemiluminescence emitter. The emission of light by this emitter was described previously for a number of other systems in chemical and electrochemical reactions[4–8] and has been attributed to two forms of redox reactions [eqns. (1) and (2)].

$$Ru^{I} + \text{oxidant} \rightarrow Ru^{II*} \rightarrow Ru^{II} + h\nu \qquad (1)$$

$$Ru^{III} + \text{reductant} \rightarrow Ru^{II*} \rightarrow Ru^{II} + h\nu \qquad (2)$$

We attribute the appearance of the chemiluminescence to the reactions of the intermediate in the process involving Ru^{III}. Taking into account the available data[1] on dark processes, we put forward Scheme 1 for the generation of chemiluminescence on dissolution of HTSC in solutions of acids.

$$YBa_2Cu_3O_{7-x} + 14H^+ \rightarrow Y^{III} + 2Ba^{II} + Cu^{III} + 2Cu^{II} + 7H_2O \qquad (3)$$

$$Cu^{III} + H_2O \rightarrow Cu^{II} + H^+ + O_2 \qquad (4)$$

$$Cu^{III} + Ru^{II} \rightarrow Cu^{II} + Ru^{III} \qquad (5)$$

$$Ru^{III} + H_2O \rightarrow [Ru^{II}]^* + H^+ + O_2 \qquad (6)$$

$$[Ru^{II}]^* \rightarrow Ru^{II} + h\nu \qquad (7)$$

$$[Ru^{II}]^* + \text{quenching agents } (Cu^{II}) \rightarrow Ru^{II} + Q \qquad (8)$$

Scheme 1

As a result of the dissolution of the HTSC, part of the copper dissolves in the form of Cu^{III} [eqn. (3)], which, apart from the familiar water oxidation reaction (4), oxidises ruthenium to Ru^{III} [reaction (5)]. The light-induced stage of the process involves reduction of the ruthenium with formation of the excited ruthenium(II) complex *via* reaction (6). The heat supplied by the water oxidation reaction (6) (2.5 eV) is quite sufficient for the generation of the excited triplet level of Ru^{II} (2.1 eV). The identification of the light-induced stage is supported by an independent observation of chemiluminescence (having the same spectrum) in the spontaneous reduction of Ru^{III} in 0.5 mol dm^{-3} H_2SO_4. According to Grazhulene and Karpov,[1] the rate of dissolution of the HTSC is higher in HCl than in H_2SO_4, but the chemiluminescence is brighter in the H_2SO_4 solution. Under these conditions, the intensity of the Ru^{II} photoluminescence after dissolution of the HTSC in solutions of both acids is the same. Two hypotheses are available to account for the brighter chemiluminescence in H_2SO_4. The high rate of dissolution in HCl ensures the generation in the solution of a higher concentration of Cu^{II} which is an effective quenching agent for $[Ru^{II}]^*$, according to Demass and Addington.[9] The quenching effect in HCl is therefore manifested by a decreased chemiluminescence. Naturally, the Cu^{III} concentration and, hence, the Ru^{III} concentration are also higher in HCl. However, the consequent increase in the amount of light cannot compensate for the decreased chemiluminescence, *i.e.* the light-induced stage (4) is the slowest and cannot compete with the quenching agent formation stage (1). We associate the second hypothesis with the formation in H_2SO_4 of a $BaSO_4$ deposit which can catalyse chemiluminescent reactions of the Ru^{II} complex. A similar effect involving the catalytic intensification of the chemiluminescence of a Ru^{II} complex on other freshly formed crystals was described previously.[5]

The much greater total light emitted on dissolution of the specimen containing more Cu^{III} ($HTSC_1$) compared with the $HTSC_2$ specimen, which has a low content of trivalent copper (the ratio of the corresponding total amounts of light is 40:1), serves as a criterion of the applicability of the observed chemiluminescence for the determination of the presence of Cu^{III} in HTSC.

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† *Experimental procedure*: $HTSC_1$ ($YBa_2Cu_3O_{6.9}$) and $HTSC_2$ ($YBa_2Cu_3O_{6.26}$) were prepared by the method of Kishio *et al.*[2] The Cu^{III} content in the HTSC (5.5% for $HTSC_1$ and <0.05% for $HTSC_2$) was determined iodometrically,[1] while oxygen was estimated by a thermodynamic procedure.[3] Solutions of $[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)_3]^{3+}$ (henceforth referred to as Ru^{II} and Ru^{III}) in 0.5 mol dm^{-3} HCl or H_2SO_4 were obtained as described by Tokel and Bard.[4] Samples of the $HTSC_1$ and $HTSC_2$ powders were placed on the optically transparent base of the chemiluminescence cell. The powder was dissolved under an argon atmosphere in an acid Ru^{II} solution and the chemiluminescence arising under these conditions was measured on the apparatus described previously.[5] Photoluminescence spectra were recorded on a Hitachi MPF-4 spectrofluorimeter.

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