Commentationes

Excited States in the Photochemistry of Chromium(III) Complexes*

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Experimental data for chromium(III) complex ions on the spectroscopic properties, photoreactions, and intermolecular energy transfer are analyzed in terms of the primary photophysical and photochemical processes. It is suggested that the lowest excited quartet state, \(4T_{2g}\) in \(O_h\) symmetry, is the immediate precursor to photoaquation and that the lowest doublet state, \(2E\), is substitution inert except via the \(4T_{2g}\) state reached by back intersystem crossing.

In the investigation of photochemical reactions of chromium complexes, particularly with reference to primary processes, definitive information about the role of excited states cannot be obtained from studies of the photochemistry alone. Recourse must be made to other techniques such as spectral measurements, quenching and energy transfer reactions, and kinetic spectroscopy, in order to sort out complexities of the primary photochemical and photophysical processes.

Solutions of octahedral chromium(III) complexes are known to undergo such photochemical reactions as: aquation, anation, racemization and isomerization [1–3]. Unlike many other transition metal complexes, those of chromium(III) generally are not susceptible to photochemical oxidation-reduction reactions.

In the following, we shall describe the photochemical reactions of some chromium(III) complexes in terms of what is known about the excited electronic states: their energies, lifetimes, quenching, etc. The available information will then be used to assess the role of the various excited states in the photochemical reactions.

* Dedicated to the memory of Professor Hans-Ludwig Schläfer.
Absorption spectra furnish a basic understanding of the low-lying excited states which may be reached in the course of a photochemical reaction of an octahedral complex [4, 5]. A typical absorption spectrum, that of \([\text{Cr(NH}_3\text{)}_6]\)\(^{3+}\), is shown in Fig. 1 [6]. The main features of such spectra are: in the red region (700 to 820 nm) a set of sharp lines of low intensity assigned to the transition \(2E_g \leftrightarrow 4A_{2g}\) (in octahedral symmetry) and other spin-forbidden transitions; in the visible region two (or sometimes three) broad structureless bands of relatively low intensity (\(e_{\text{max}}\) of the order of 50 \(M^{-1}\text{cm}^{-1}\)), representing the Laporte forbidden transitions \(4T_{2g} \leftrightarrow 4A_{2g}\) and \(4T_{1g} \leftrightarrow 4A_{2g}\); and, usually in the UV and near UV region of the spectrum, a number of intense bands which are intraligand and/or charge-transfer bands.

In emission spectra, two types of transitions have been observed: phosphorescence, \(2E_g \rightarrow 4A_{2g}\), and fluorescence, \(4T_{2g} \rightarrow 4A_{2g}\) [7, 8]. No other emission has been reported for chromium(III) complexes, although charge-transfer and intraligand transitions have been characterized from the emission spectra of other transition metal complexes [8]. Usually, phosphorescence is the only emission which can be readily observed, and then best at low temperatures, but there are some cases for which fluorescence emission is comparable in intensity with the phosphorescence and still others which show only fluorescence [9]. Which of these occur has been correlated with the relative energies of the \(2E_g\) and \(4T_{2g}\) states [10].

Phosphorescence spectra, like the corresponding absorption spectra, consist of a set of sharp lines, one of which occurs strongly in both absorption and emission and represents the origin of the band or the zero-zero transition. Other lines in the spectra are vibronic in nature and lie to the blue of the origin in absorption and to the red of the origin in emission except for “hot” bands originating in excited vibrational levels. The fluorescence spectra, on the other hand, are invariably broad and structureless (except possibly at 4 \(^\circ\text{K}\) in

![Fig. 1. Absorption spectrum of \([\text{Cr(NH}_3\text{)}_6]\)\(^{3+}\)