Inorganica Chimica Acta, 16 (1976) L5 - L6

Radiative Lifetimes of Some Cr(III) Ammines under Photochemical Conditions

A. W. ADAMSON, C. GEOSLING, R. PRIBUSH, and R. WRIGHT

Department of Chemistry, University of Southern California, Los Angeles, California 90007, U.S.A.

Received September 19, 1975

We wish to report measurements on the phosphorescence lifetimes of $Cr(en)_3^{3+}$, $Cr(NH_3)_6^{3+}$, and $Cr(bipyr)_3^{3+}$ (bipyr = 2,2'-bipyridine) in room temperature aqueous solution. The exciting radiation was at 530 nm, provided by a Nd glass oscillator, Q-switched, amplified, frequency doubled, and filtered to remove 1060 nm radiation. The pulses were in the range of 0.1 J, as determined by reineckate actinometry,[1] or of sufficient energy to produce about 0.5% photolysis per pulse. The pulse halfwidth time was about 20 nsec; relative pulse energies were obtained by means of a photodiode and interating circuit. A red sensitive photomultiplier provided the output for voltage–time oscilloscope traces, which were photographed and transcribed to graph paper. The emission was observed through a set of Corning red filters cutting off below 650 nm, and was corrected for the output seen with water only in the cell.

The emission decay plots are shown in the Figure. Each set of points is adjusted to a standard pulse energy and, since the emission intensity scale is relative, the origins of the various plots are adjusted for clarity of presentation. Concentrations were about 10^{-4} *M*, chosen so as to give as much emission intensity as possible consistent with not saturating the photomultiplier. The complexes were recrystallized and were spectrally pure from comparisons with literature visible absorption spectra. Solutions were in distilled water at the natural pH, and were filtered.

Our observed lifetime for the $Cr(en)_3^{3+}$ phosphorescence is 1.3 μsec, in agreement with the value of 1.33 μsec reported by Ballardini *et al.*[2] for about the same temperature and medium. The values of 1.8 μsec for $Cr(NH_3)_6^{3+}$ and 45 μsec for $Cr(bipyr)_3^{3+}$ are new, although the presence of emission had been reported earlier.[3] We were unable to detect emission from $Cr(urea)_6^{3+}$, $Cr(NCS)_3^{3+}$, or *trans*-$Cr(NH_3)_2(NCS)_4^-$ (Reinecke's salt), although weak to very weak emissions had been reported for the last two.[3]

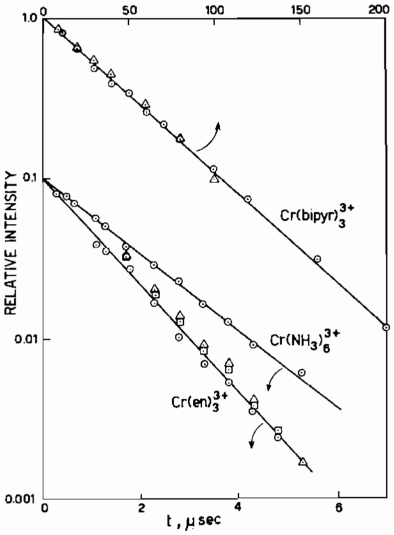

Figure 1. Upper plot (and upper abscissa scale): $Cr(bipyr)_3^{3+}$. Lower plots (and lower abscissa scale): $Cr(NH_3)_6^{3+}$, $Cr(en)_3^{3+}$. The different sets of points represent separate runs.

It has been inferred (with some assumptions) that much of the photoaquation of $Cr(en)_3^{3+}$ occurs from a thermally equilibrated or thermodynamic excited (thexi) quartet state, by molecules that have passed through the first doublet thexi state. To the extent that these two thexi states are in thermal equilibrium, their decay times should be the same; measurement of the phosphorescence lifetime thus indicates the lifetime of the reacting quartet state. It is therefore of potential interest that with the present data we can now compare lifetimes and quantum yields for three complexes, measured under essentially the same conditions. The photoaquation yields for $Cr(en)_3^{3+}$, $Cr(NH_3)_6^{3+}$, and $Cr(bipyr)_3^{3+}$ are about 0.45,[2,4] 0.30,[4] and *ca.* 0.003,[5] respectively. It might be expected that the longer lived system might have the larger aquation yield because of lesser competition from non-radiative deactivation, but this is not the case. In the framework of assuming rapid equilibrium between the doublet and quartet thexi states, aquation from promptly formed latter state appears to be an important but not predominant complication.[2] On this basis we may infer approximate values for the rate constants for chemical reaction k_{cr}, and for non-reactive deactivation, k_{nr}, of the quartet thexi state. The relationships are $\tau = 1/(k_{cr} + k_{nr})$, $\phi = \tau k_{cr}$ where τ and ϕ are lifetime and quantum yield, respectively. We thus estimate $k_{cr} = 3.5 \times 10^5$, 1.7×10^5, and 67 in sec^{-1} and $k_{nr} = 3.2 \times 10^5$, 3.9×10^5, and 2.2×10^4 in sec^{-1}, for $Cr(en)_3^{3+}$, $Cr(NH_3)_6^{3+}$. and $Cr(bipyr)_3^{3+}$. respectively. It appears that major variations occur in both rate constants. The assumption of thermal equilibrium between thexi states may not be correct, however; it is hoped, in work under way, to measure k_{cr} directly by observing the rise time of product formation using high energy laser pulse photolysis.

Some unexplored complexities are that the quantum yield for the photoaquation of $Cr(bipyr)_3^{3+}$ is pH dependent, increasing with acidity,[5,6] there may be a pH effect on τ. Also, it was observed for $Cr(NH_3)_6^{3+}$ that addition of a filter cutting off emission of longer than about 700 nm wavelength made the emission non-exponential; the 1.8 μsec component was greatly reduced in intensity and a faster and possibly also a more slowly decaying component appeared to be present. This behavior is under further study.

Acknowledgments

We are very grateful to Professor E. Eyring of the University of Utah for allowing our group use of his laser facility and to the U.S. Office of Naval Research for facilitating the arrangements. We acknowledge support from the latter agency and from the U.S. Army Research Office (Durham) and the U.S. National Science Foundation.

References

1 E. E. Wegner and A. W. Adamson, *J. Am. Chem. Soc., 88,* 394 (1966).

2 R. Ballardini, G. Varoni, H. F. Wasgestian, L. Moggi, and V. Balzani, *J. Phys. Chem., 77,* 2947 (1973).

3 N. A. P. Kane-Maguire and C. H. Langford, *Chem. Comm.,* 895 (1971).

4 V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds", Academic Press, 1970.

5 R. Wright and A. W. Adamson, unpublished work.

6 V. Balzani, private communication.