Inorganica Chimica Acta, 144 (1988) 53–55

On the Excited State Disproportionation of $Ru(bipy)_3^{2+}$

G. FERRAUDI* and G. A. ARGÜELLO

Radiation Laboratory, University of Notre Dame, Notre Dame, Ind. 46556, U.S.A.

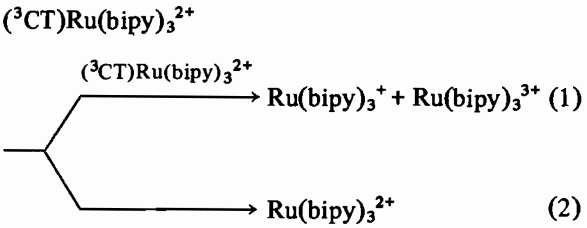
(Received June 23, 1987)

Abstract

The disproportionation of $(^3CT)Ru(bipy)_3^{2+}$ in homogeneous solutions has been investigated by laser flash photolysis where excitations were carried out with high intensities ($250 > I_{ab} > 70$ MW/cc) of monochromatic light ($\lambda_{excit} \sim 440$ nm). Such a disproportionation reaction competes, at a nearly diffusion-controlled rate, with the unimolecular (radiation and radiationless) relaxation.

Introduction

It has been predicted that the disproportionation of $(^3CT)Ru(bipy)_3^{2+}$, eqn. (1), should be able to compete with the unimolecular relaxation of the excited species, eqn. (2) [1].



$$(^3CT)Ru(bipy)_3^{2+} \xrightarrow{(^3CT)Ru(bipy)_3^{2+}} Ru(bipy)_3^{+} + Ru(bipy)_3^{3+} \quad (1)$$

$$(^3CT)Ru(bipy)_3^{2+} \longrightarrow Ru(bipy)_3^{2+} \quad (2)$$

Some evidence about the disproportionation reaction has been reported for $Ru(bipy)_3^{2+}$ adsorbed in cellulose; a medium that highly limits the use of chemical scavengers [2]. By contrast, the triplet–triplet annihilation, eqn. (3), in polyelectrolyte or ion exchanger media has been proposed as a justification of mixing first and second order kinetics, in the kinetics of the excited state relaxation [3, 4].

$$2(^3CT)Ru(bipy)_3^{2+} \longrightarrow (^1CT)Ru(bipy)_3^{2+} + Ru(bipy)_3^{2+} \quad (3)$$

Moreover, experiments carried out in homogeneous solutions, under conditions where one would hope to observe the excited state disproportionation, *i.e.* flash photolysis with high intensity polychromatic light, induce sequential biphotonic processes, eqns. (4) and (5) [5].

$$Ru(bipy)_3^{2+} \xrightarrow{h\nu} (^3CT)Ru(bipy)_3^{2+} \xrightarrow{h\nu} Ru(bipy)_3^{3+} + e_{aq}^{-} \quad (4)$$

$$e_{aq}^{-} + Ru(bipy)_3^{2+} \longrightarrow Ru(bipy)_3^{+} \quad (5)$$

Insofar as some of these studies were done under rather limiting experimental conditions, discrimination between the bimolecular reactions, eqns. (1) and (3), is rather difficult in particular, when one considers complications introduced by the biphotonic reaction, eqns. (4) and (5). One way to circumvent such quandaries is to use specific scavengers of the solvated electron, eqns. (4) and (5), while monitoring the concentration of Ru(I) species in flash photochemical experiments. In this work, we report results supporting a significant disproportionation of the excited state in homogeneous aqueous solutions.

Results and Discussion

Flash irradiations of the ruthenium complex ($5.0 \times 10^{-4} > [Ru(bipy)_3^{2+}] > 10^{-5}$ M) in deaerated aqueous acidic ($2 < pH < 5$) solutions with high intensity ($\lambda_{excit} = (440 \pm 10)$ nm and $250 > I_{ab} > 70$ MW/cc) produce transient spectra corresponding to the generation of $Ru(bipy)_3^{+}$ and $Ru(bipy)_3^{3+}$ within the excited state lifetime†. Inspection of the spectral transformations at 450 or 500 nm, Fig. 1, reveals that $Ru(bipy)_3^{+}$ is formed with significant yields in solutions containing scavengers of the solvated electron, e.g. H^+ and N_2O. For example, the yield of

---

*Author to whom correspondence should be addressed.

†The yield of $Ru(bipy)_3^{+}$ shows a complex dependence on the concentration of $Ru(bipy)_3^{2+}$ which reflects the relationship of this experimental variable to the intensity of absorbed light and local concentration of excited state. In a limit $[Ru(bipy)_3^{2+}] > 5 \times 10^{-4}$ M, solutions were too concentrated leading to optical distortions in the detection. The information derived from these experiments was regarded as inconclusive for the establishment of a reaction mechanism.

0020-1693/88/$3.50

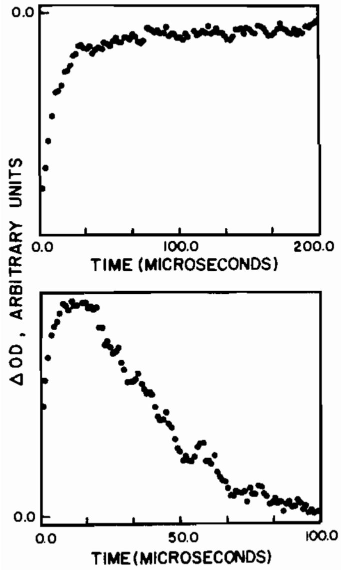


Fig. 1. Traces recorded in the (^{3}CT)Ru(bipy)$_3^{2+}$ disproportionation: bleaching of the 450 nm optical density (top) and 500 nm transient absorption (bottom) observed in high intensity (250 MW/cc) irradiations of 5.0×10^{-4} M Ru(bipy)$_3^{2+}$.

TABLE I. Yields of Ru(bipy)$_3^+$ from Excited State Disproportionation

pH	[Ru(bipy)$_3^+$] × 10^5 (M)$^{a, b}$
2.0	1.2
4.2	1.5
5.8	1.8

^{a}Values of Ru(I) concentration determined with $I_{ab} \sim 250$ MW/cc in 440 nm excitations of solutions deaerated with N_2 streams. Ionic strength 0.1 M adjusted with NaClO$_4$. ^{b}Concentrations produced per pulse. Each figure represents an average of 10–20 determinations.

Ru(bipy)$_3^+$ is largely pH independent, Table I, and laser flash irradiations of *ca.* 10^{-4} M Ru(bipy)$_3^{2+}$ in deaerated solutions containing either 10^{-2} M HClO$_4$ or 2.5×10^{-2} M N_2O at pH 4 resulted in similar yields of the Ru(bipy)$_3^+$ product. Insofar as the solvated electron reacts 39 times faster with H^+ (at pH 2) and 40 times faster with N_2O (at pH 4) than with Ru(bipy)$_3^{2+}$, the biphotonic mechanism of Ru(bipy)$_3^+$ formation, eqns. (4) and (5), cannot correctly account for our results*. The mechanism considering the bimolecular disproportionation of the excited state, eqns. (1) and (2), gives a better description of the Ru(bipy)$_3^{2+}$ high intensity photochemistry in agreement with the reported experiments in cellulose [2]. In this mechanism and under the experimental conditions used in this work, we estimated that the disproportionation, eqn. (1), must compete, at nearly a diffusion controlled rate, with the first order relaxation, eqn. (2)**. It is possible, therefore, that in homogeneous solutions with low flash intensities, *i.e.* $I_{ab} < 70$ MW/cc, such a reaction has passed undetected while high intensities of polychromatic light, *i.e.* in conventional flash photolysis, led to biphotonic processes. On the other hand, our results raise serious doubts about the significance of the triplet–triplet annihilation, eqn. (3), in particular when such a proposition is based only on time-resolved emission studies, [3, 4, 7].

Experimental

Photochemical Procedures

Flash photolysis studies were carried out in an apparatus previously used for the investigation of sequential biphotonic photochemistry [8]. In the experiments described here, one of the flash-lamp-pumped dye lasers (Candela SLL-200) was used with appropriate dyes for excitations at 440 nm of solutions deaerated with streams of ultra high purity N_2.

Materials

[Ru(bipy)$_3$]Cl$_2$ from Alfa was transformed to the perchlorate salt and purified with three consecutive recrystallizations from aqueous solutions by the addition of solid NaClO$_4$. Other chemicals were reagent grade and used without further purification.

Acknowledgement

The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2958 from the Notre Dame Radiation Laboratory.

References

1 C. Creutz and N. Sutin, *J. Am. Chem. Soc.*, *98*, 6384 (1976).
2 B. H. Milosavijevic and J. K. Thomas, *J. Phys. Chem.*, *87*, 616 (1983).

---

*Rate constants for the calculations were extracted from ref. 6.

**This value for the second order disproportionation rate constant is in acceptable agreement with the one reported in cellulose, $k \sim 10^8$ M^{-1} s^{-1}, when one considers the medium differences [2].

3 S. Kelder and J. Rabani, *J. Phys. Chem.*, *85*, 1637 (1981).

4 A. Slama-Schwok, Y. Feitelson and J. Rabani, *J. Phys. Chem.*, *85*, 2222 (1981).

5 D. Meisel, M. S. Matheson, W. A. Mulac and J. Rabani, *J. Phys. Chem.*, *81*, 1449 (1977).

6 M. Ambar, M. Bambenek and A. B. Ross, *Nat. Stand. Ref. Data Ser., No. 43*, National Bureau of Standards, Washington, D.C., 1973.

7 S. Wei, H. D. Gafney, J. B. Clark and D. J. Peretti, *Chem. Phys. Lett.*, *99*, 253 (1983).

8 B. Van Vlierberge and G. Ferraudi, *Inorg. Chem.*, *26*, 337 (1987).