affinity by ca. $3 \times 10^3$, and the additional decrease in affinity of roughly 15-fold arises almost entirely from a reduction in the on-rates. Since proximal strain affects on and off rates equally, this suggests that other or additional mechanisms must be invoked. For example, steric hindrance on the heme distal side lowers the CO on-rate without affecting the off-rate.[6a,21] The lowered affinity of the T-state model more closely approaches that of the T state in the absence of IHP, but even in this case, the protein affinity is moderately lower (~4-fold) and the difference results primarily from a reduction in on rates. The level of success of the 2-MeIm-heme model for the T state may reflect a contribution of proximal strain or may be accidental, with the effects of this strain merely mimicking one or more of other postulated mechanisms.[6,7,21,22] In any case, a heme model does not yet exist that entirely reproduces the plasticity of hemoprotein ligation.

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## Oscillating Chemiluminescence from the Reduction of Bromate by Malonic Acid Catalyzed by Tris(2,2′-bipyridine)ruthenium(II)

Fabrizio Bolletta* and Vincenzo Balzani*

*Istituto Chimico "G. Ciamician" dell'Università*
*and Istituto FRAE/CNR, Bologna, Italy*

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We report the observation of oscillating chemiluminescence during the Belousov–Zhabotinskii (BZ) reaction[1,2] (reduction of bromate by malonic acid) when tris(2,2′-bipyridine)ruthenium(II), Ru(bpy)$_3^{2+}$, is used as a catalyst. The oscillating chemiluminescence, which is due to the reduction of Ru(bpy)$_3^{3+}$ by some strongly reducing radical with formation of the emitting excited state of Ru(bpy)$_3^{2+}$, shows a very peculiar time behavior. To our knowledge this is the first example of oscillating chemiluminescence in solution.

It is well established that certain types of chemical reactions, subject to appropriate conditions, organize themselves spontanesously to give rise to regular spatial patterns or to periodic rate fluctuations.[1-6] The best studied among the oscillating homogeneous processes is the "classical"[7] BZ reaction, in which a crucial role is played by an ox/red catalyst.[1-14] The usual catalyst of the BZ reaction is the Ce$^{4+}$/Ce$^{3+}$ couple, but the Mn$^{3+}$/Mn$^{2+}$ couple[6] and polypyridine complexes of Fe,[8,12] Ru,[8,15] Ag,[16] Os,[17] and Cr[17] have also been used. The stoichiometry of the overall process is thought to be that of eq 1. The mechanism involves

$$2\mathrm{BrO_3^-} + 3\mathrm{CH_2(COOH)_2} + 2\mathrm{H^+} \xrightarrow{\mathrm{ox/red}} 2\mathrm{BrCH(COOH)_2} + 3\mathrm{CO_2} + 4\mathrm{H_2O} \quad (1)$$

oxidation of the reduced form of the catalyst (red) by bromate and reduction of the oxidized form of the catalyst (ox) by malonic acid. Each of these mechanistic stages is complicated and involves many steps, some of which could be different when different catalysts are used.[7,8,12] With Ru(bpy)$_3^{2+}$ as a catalyst, oscillations had been previously observed in the rate of heat evolution,[8] in the rate of accumulation of monobromomalonic acid,[8] and in the UV-induced Ru(bpy)$_3^{2+}$ photoluminescence.[15]

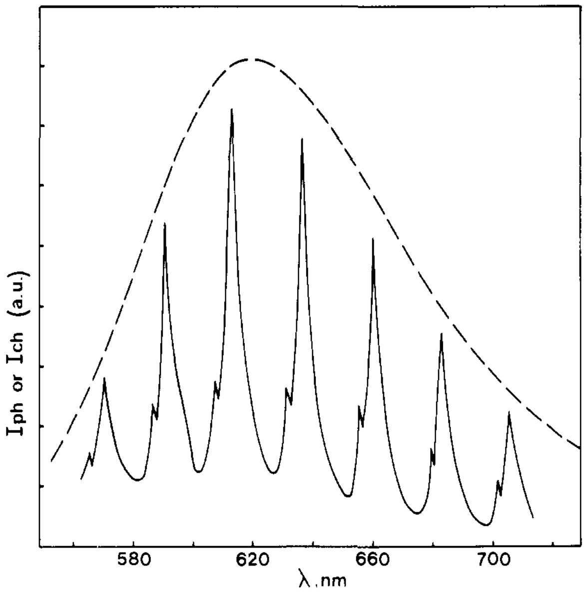

**Figure 1.** Oscillating chemiluminescence emission spectrum of the Ru(bpy)$_3^{2+}$-catalyzed BZ reaction (—) compared with the photoluminescence spectrum of Ru(bpy)$_3^{2+}$ (---) recorded by an MPF-3 Perkin-Elmer fluorimeter. Experimental conditions for chemiluminescence emission: KBrO$_3$, 0.06 M; malonic acid, 0.25 M; H$_2$SO$_4$, 1.5 M; Ru(bpy)$_3^{2+}$, $1.0 \times 10^{-4}$ M; slit, 40 nm; sensitivity, ×30.

In the last few years Ru(bpy)$_3^{2+}$ and other transition-metal complexes of the polypyridine family have been the object of much interest because of their peculiar photochemical and photophysical properties.[18-21] In particular, these complexes have been extensively used as light-absorption sensitizers[19-22] in artificial systems for the conversion of solar energy into chemical and/or electrical energy and as light-emission sensitizers[23-27] in artificial systems for the conversion of chemical and/or electrical energy into light.[28] The standard reduction potential of the Ru(bpy)$_3^{3+}$/Ru(bpy)$_3^{2+}$ couple in aqueous solution is +1.26 V vs. NHE, and the luminescent excited state of Ru(bpy)$_3^{2+}$, *Ru(bpy)$_3^{2+}$, is known to lie 2.12 eV above the ground state.[19-21] Thus, when Ru(bpy)$_3^{3+}$ is reduced by a reductant R$^-$ having $E^0(\mathrm{R/R^-}) < -0.86$ V, either the ground state (eq. 2) or the excited state (eq

$$\mathrm{Ru(bpy)_3^{3+}} + \mathrm{R^-} \rightarrow \mathrm{Ru(bpy)_3^{2+}} + \mathrm{R} \quad (2)$$

$$\mathrm{Ru(bpy)_3^{3+}} + \mathrm{R^-} \rightarrow {}^*\mathrm{Ru(bpy)_3^{2+}} + \mathrm{R} \quad (3)$$

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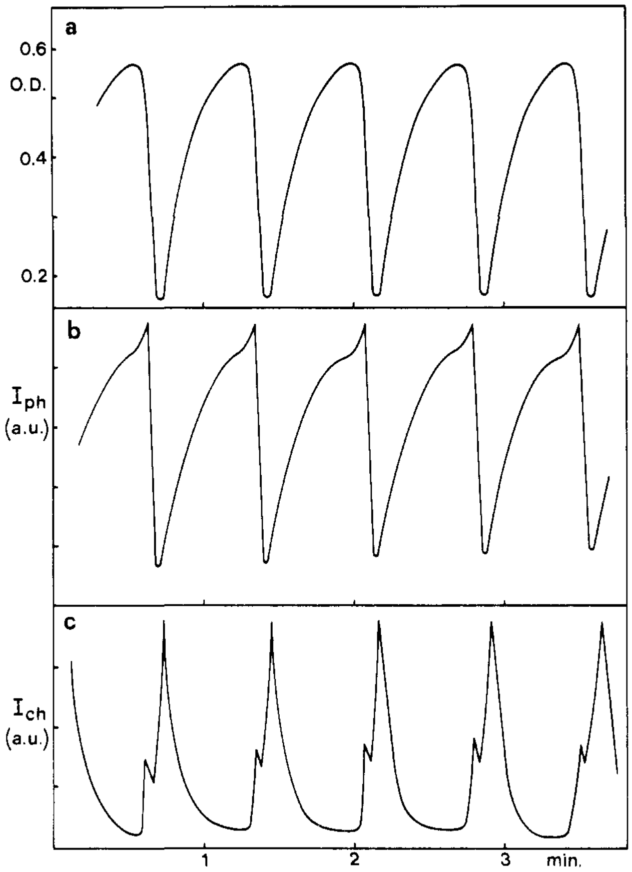

**Figure 2.** Oscillating light absorption at 450 nm (a), oscillating photoluminescence emission at 610 nm (b), and oscillating chemiluminescence emission at 610 nm (c) in the $Ru(bpy)_3{}^{2+}$-catalyzed BZ reaction. Experimental conditions are as in Figure 1.

3) of $Ru(bpy)_3{}^{2+}$ can be obtained. Actually, when both reactions 2 and 3 are thermodynamically allowed, reaction 3 predominates for kinetic reasons,[24] and since the quantum yield of $*Ru(bpy)_3{}^{2+}$ emission is high,[24] luminescence can be easily observed. Rubinstein and Bard[25] have recently shown that chemiluminescence can be obtained when organic acids are oxidized by $Ru(bpy)_3{}^{3+}$ or in the presence of $Ru(bpy)_3{}^{2+}$. The reaction mechanism involves reduction of $Ru(bpy)_3{}^{3+}$ by strongly reducing radicals generated in the one-electron oxidation of the organic acid. We have observed that chemiluminescence is also obtained on mixing aqueous solutions of $Ru(bpy)_3{}^{3+}$ and malonic acid in 1 M $H_2SO_4$. Since the $Ru(bpy)_3{}^{3+}$ concentration oscillates[8,15] in the BZ reaction and since a large concentration of malonic acid is also present, we thought that the oscillating reaction has to be accompanied by an oscillating chemiluminescence emission. When an aqueous solution containing 0.25 M malonic acid, 0.06 M $KBrO_3$, 1 M $H_2SO_4$, and $1.0 \times 10^{-4}$ M $Ru(bpy)_3{}^{2+}$ was examined for chemiluminescence in a fluorimeter, an oscillating signal was indeed recorded, although the light emission was too weak to be observed by eye.

Subsequent systematic investigations showed that (i) the chemiluminescence spectrum is identical (except for oscillations) with the photoluminescence spectrum of $Ru(bpy)_3{}^{2+}$ (Figure 1), (ii) the intensity and period of the oscillating chemiluminescence depend on the reactant concentrations and decrease with time, and (iii) the oscillating chemiluminescence has the same period but is out of phase compared with the oscillating light absorption at 450 nm (where the extinction coefficient of $Ru(bpy)_3{}^{2+}$ is much higher than that of $Ru(bpy)_3{}^{3+}$) and with the oscillating photoluminescence emission (which is due to $Ru(bpy)_3{}^{2+}$ absorption) (Figure 2).

The shapes of the oscillating curves shown in Figure 2 merit some comments. The shape of the light absorption oscillation (Figure 2a) shows that the interconversion of $Ru(bpy)_3{}^{2+}$ and $Ru(bpy)_3{}^{3+}$ is due to a smooth reaction. By contrast, the photoluminescence oscillation (Figure 2b) shows a shoulder and then a sharp peak before decreasing. These features cannot be due to concomitant variations in the $Ru(bpy)_3{}^{2+}$ concentration because in such a case they should also appear in the light absorption oscillation curve of Figure 2a. In the same way, we can note that the chemiluminescence curve (Figure 2c) exhibits an oscillatory behavior that does not exactly reflect the changes in the $Ru(bpy)_3{}^{3+}$ concentrations shown by Figure 2a. We believe that the peculiar features of the photoluminescence and chemiluminescence curves are due to the oscillating formation of radical species which may act as quenchers for $*Ru(bpy)_3{}^{2+}$ and as reactants for the $Ru(bpy)_3{}^{3+}$ chemiluminescent reaction. A more thorough investigation of this system might reveal new details of the mechanism of the BZ reaction.

Other experiments on this artificial "firefly" system are in progress in our laboratory.

**Registry No.** $Ru(bpy)_3{}^{2+}$, 15158-62-0; $BrO_3{}^-$, 15541-45-4; malonic acid, 141-82-2.

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## Chiral Total Synthesis of Compactin

Masahiro Hirama* and Mitsuko Uei

*Suntory Institute for Bioorganic Research*
*Shimamoto-cho, Mishima-gun, Osaka 618, Japan*

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Compactin[1a] (from *Penicillium brevicompactum*) [or ML-236B[1b] (from *P. citrinum*), **1a**], monacolin K[2a] (or mevinolin,[2b] **1b**), and dihydro compounds **2a** and **2b**,[3] which are potent inhibitors of 3-hydroxy-3-methylglutaryl coenzyme A (HMG-CoA) reductase, have attracted considerable interest because of their high hypocholesterolemic activity.[4] This important family of polyketide-derived compounds possesses a highly functionalized hexahydronaphthalene (or *trans*-octalin) skeleton substituted with a $\beta$-hydroxy $\delta$-lactone moiety.

In this communication, we report an enantioselective and convergent synthesis of **1a**,[5] which is also adaptable to the synthesis of the other related compounds **1b**, **2a**, and **2b**. Our synthetic strategy outlined in Scheme I encompasses several interesting synthetic facets. (1) The intramolecular Diels–Alder reaction of **4** via exo orientation was considered to be a viable approach for the construction of the *trans*-octalone system **3**, since deca-1,7,9-trien-3-one cyclized exclusively to *trans*-octalone.[6] (2) The concomitant asymmetric induction of four asymmetric centers, C8, C9, C14, and C17 in **3**, might be realized in this [4 + 2]

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