Chemiluminescence Energy Transfer Reaction for the On-Line Preparation of Peroxymonocarbonate and Eu(II)—Dipicolinate Complex

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In this work, an on-line preparation of peroxymonocarbonate was formed innovatively, which offered a reliable intermediate for further investigation. The forming conditions of on-line peroxymonocarbonate ions were investigated in detail. Meanwhile, the energy transfer chemiluminescent reaction of peroxymonocarbonate and the Eu(II)—dipicolinate complex was studied. Through UV—visible absorption spectra, CL method, ESR spin-trapping technique, and mass spectrum experiments, it can be concluded that peroxymonocarbonate oxidizes Eu(II) to Eu(III), and simultaneously creates radicals. The bond rearrangement within radicals formed the singlet molecular oxygen. The energy originating from the singlet oxygen was accepted by the (Eu(III)dipic) complex. The excited (Eu(III)*dipic) ions underwent radiative deactivation and emitted the chemiluminescence. The peroxymonocarbonate system was a simple, inexpensive, and relatively nontoxic alternative to other oxidants, and it can be used in a mild, neutral-pH environment.

1. Introduction

Carbonate or bicarbonate has often been used as buffer solution for the chemiluminescence (CL) medium. Much research1–5 has indicated that carbonate or bicarbonate acted not only as a buffer reagent but also as the CL enhancer. It has been confirmed that CO$_3^{2-}$ was a luminous species when it coexisted with a strong oxidant in basic solution. In our previous works,3,5 a possible CL mechanism was suggested in which the CO$_3^{2-}$/HCO$_3^-$ ions were attacked by superoxide radicals which generated carbonate free radicals (CO$_3^*$). Then, CO$_3^*$ recombined to generate excited triplet dimers of two CO$_2$ molecules (1$^2$CO$_2$). With the decomposition of this unstable intermediate to CO$_2$, the energy was released and the CL was emitted. Recently, an interesting research work, the formation of a bicarbonate active species, peroxymonocarbonate (HCO$_4^-$), was reported.6 It was discovered that the equilibrium of hydrogen peroxide and bicarbonate to form HCO$_4^-$ occurred rapidly at 25 °C near neutral pH in aqueous solution or ethanol/water mixtures (eq 1).

\[ \text{HCO}_3^- (\text{solv}) + \text{H}_2\text{O}_2 (\text{solv}) \rightarrow \text{HCO}_4^- (\text{solv}) + \text{H}_2\text{O} (\text{solv}) \]

Such equilibrium had previously been observed by Richardson’s group,7 and HCO$_4^-$ without metal ion was found to be a moderately reactive heterolytic oxidant that can be classified as an anionic peracid.8 The effective equilibrium constant $K_1 = 27 \pm 1$ at 25 °C was observed, and the observed equilibration rate constant was $(2.4 \pm 0.1) \times 10^{-3}$ s$^{-1}$.9 The half-life for formation of HCO$_4^-$ in ethanol/water (1.76:1, v:v) was about 300 s, and the electrode potential for the HCO$_2^-$ / HCO$_3^-$ couple was $1.8 \pm 0.1$ V vs NHE. From these data, it can be concluded that it was suitable to select ethanol/water as the solvent, which shifted the equilibrium of eq 1 to the right, and favoring increased formation of peroxymonocarbonate ion. Recent experiments reported by Richardson et al.6 showed that increases in catalytic efficiency of the bicarbonate—peroxide system could be achieved by using a more soluble source of ammonium bicarbonate and ethanol in place of NaHCO$_3$ and tert-butyl alcohol, respectively. Meanwhile, these two data points gave us an idea that the active species HCO$_4^-$ has character similar to that of peroxymonosulfate (HSO$_5^-$), which had been used as a CL analytical reagent several years ago.9

Though there were a lot of established chemiluminescence (CL) systems for analysis applications, they suffered from one or more disadvantages, such as toxicity or release of some byproducts which were unfriendly to the environment. The peroxymonocarbonate system, bicarbonate-activated peroxide, offered a simple, inexpensive, and relatively nontoxic alternative to other oxidants. This feature made it widely used as an oxidant in many reactions,10 such as methionine,11 alkene,8,12,13 and sulfide.6,14 However, the oxidant was unstable and hydrolyzed rapidly, forming HCO$_3^-$ and H$_2$O$_2$. It was obviously difficult to store the HCO$_4^-$ ions. Hence, on-line preparation of HCO$_4^-$ was likely to be the preferable method in most applications. Furthermore, the CL systems with HCO$_4^-$ as oxidant were very few. To the best of our knowledge, no CL system which used HCO$_4^-$ as oxidant has been reported. Thus, it is desirable to exploit the CL system. In this work, the flow analysis technique was used to introduce a continuous flowing stream without a gap into the channel. At the same time, by using the peristaltic pump, it was easy to go along a multichannled stream and control the flow rate for the appropriate on-line formation time. Through a three-way piece, the two streams (H$_2$O$_2$ in ethanol/water (1.76:1, v:v) binary solvents and HCO$_3^-$) could be injected into the flow cell. The half-life of the HCO$_4^-$ ions in ethanol/water corresponded to an increasing amount of HCO$_4^-$. Therefore, it was an idea to use the HCO$_4^-$ ions as an oxidant in the CL system.
after injecting Eu(II) into the HCO₄⁻ solution; (B) the investigations of energy transfer CL.

However, using only ethanol leads to phase separation or insolubility of the salt. In our work, the ratio 1.76:1 was employed, and the concentration of NH₄HCO₃ was sufficiently low such that solubility saturation effects were not observed.

In view of the short lifetime and high activity of this active carbon oxygen intermediate, and unique luminescence properties of Eu(II) ion complexes, i.e., long luminescence decay time and narrow emission bands, Eu(II) complexes were particularly well-suited for an energy transfer study in HCO₄⁻ CL reaction. In 1983, a series of studies on CL emitted during oxidation of Eu(II) ions in complexes with organic ligands by hydrogen peroxide had begun. This reaction, involving radicals, led to the appearance of excited Eu(III) ions, and the CL intensity significantly increased after complexation of Eu(II) ions. In the present work, we found that an ultraweak CL was observed significantly increased after complexation of Eu(II) ions. In the appearance of excited Eu(III) ions, and the CL intensity employed, and the concentration of NH₄HCO₃ was sufficiently insolubility of the salt. In our work, the ratio 1.76:1 was accounted.

Schematic diagram of flow-injection CL detection system and in Figure 1. It consists of a peristaltic pump with two lines. The flow streams H₂O₂ in 1.76:1 ethanol/water solution and bicarbonate through a three-way piece. The on-line HCO₄⁻ solution was obtained by mixing H₂O₂ (in ethanol/water (1.76:1, v/v) mixture) and bicarbonate through a three-way piece. A 35 cm mixing coil was used for efficient mixing of H₂O₂ and bicarbonate. A Eu(II) solution was injected into the carrier stream (dipic) using a six-way injection valve with a 150 µL sample loop, and then, it was merged just prior to reaching a flow cell with a stream of HCO₃⁻ solution. The flow cell was a flat spiral-coiled colorless glass tube (1.0 mm i.d.; total diameter of the flow cell, 3 cm, without gaps between loops) and located directly facing the window of the CR-105 photomultiplier tube (Hamamatsu, Tokyo, Japan) operated at ~800 V. The CL signal produced in the flow cell was detected and recorded with a computerized ultraweak luminescence analyzer (type LF-800, manufactured at Microtec NITI-ON, Funabashi, Japan). Data acquisition and treatment were performed with LUM-2000 software running under Windows XP.

2. Experimental Section

2.1. Reagents and Materials. Hydrogen peroxide (30%, Alfa Aesar, U.S.A.), ammonium bicarbonate (AR), and ethanol (AR) were used without further purification. Hydrogen peroxide solution (2.0 mol/L) was prepared by diluting 20 mL of 30% (v/v) hydrogen peroxide to 100 mL with water and was standardized by potassium permanganate standard solution. Sodium bicarbonate, sodium carbonate, potassium bicarbonate, and potassium carbonate, analytical reagent, were used as received. The Eu(II) solutions used were obtained by reduction of Eu(III) ions, as a result of which the CL intensity increased significantly after complexation of Eu(II) ions. The degree of reduction of europium was determined by iodometric titration immediately prior to measurement. For ¹³C NMR studies, 98% ¹³C-enriched sodium bicarbonate (Alfa Aesar, U.S.A.) and 99.95% D₂O (Alfa Aesar, U.S.A.) were used. 2,2,6,6-Tetramethylpiperidine (98%) and 99% 9,10-diphenylanthracene (Acrós Organics, Belgium) were used.

Water was purified using a Barnstead Nanopure system (18.3 MΩ cm⁻¹, Barnstead, Iowa, U.S.A.).

2.2. Procedure for CL Detection. The schematic diagram of the flow system employed in this work is shown in Figure 1. A multichannel peristaltic pump was used to deliver all flow streams in this system. PTFE tubing (1.0 mm i.d.) was used as connection material in the flow system. The on-line HCO₄⁻ solution was prepared by mixing H₂O₂ (in ethanol/water (1.76:1, v/v) mixture) and bicarbonate through a three-way piece. A 35 cm mixing coil was used for efficient mixing of H₂O₂ and bicarbonate. A Eu(II) solution was injected into the carrier stream (dipic) using a six-way injection valve with a 150 µL sample loop, and then, it was merged just prior to reaching a flow cell with a stream of HCO₃⁻ solution. The flow cell was a flat spiral-coiled colorless glass tube (1.0 mm i.d.; total diameter of the flow cell, 3 cm, without gaps between loops) and located directly facing the window of the CR-105 photomultiplier tube (Hamamatsu, Tokyo, Japan) operated at ~800 V. The CL signal produced in the flow cell was detected and recorded with a computerized ultraweak luminescence analyzer (type LF-800, manufactured at Microtec NITI-ON, Funabashi, Japan). Data acquisition and treatment were performed with LUM-2000 software running under Windows XP.

3. Results and Discussion

3.1. On-line Preparation of HCO₃⁻ Ions. Taking into account the relative difficulty of storing the unstable HCO₃⁻, on-line preparation of HCO₃⁻ solution was likely to be the preferred method. The flow analysis method was a fast, continuous method. On the basis of discrete instant sampling by injection into a carrier stream, the system allowed continuous on-line analysis to be performed in a fast, greatly simplified way. As the continuous flowing stream was characterized by a turbulent rather than a laminar flow, the discrete instant sampling created geometically well-defined segments of sample solution within the flowing stream. It introduced a continuous flowing stream without a gap into the channel, which makes the on-line mixing true. At the same time, by using the peristaltic pump, it was easy to go along a multichanneled stream and control the flow rate for the appropriate on-line formation time. These merits guaranteed sufficient reaction time. It provided the room for on-line preparation of HCO₃⁻ ions.

The on-line HCO₃⁻ solution was obtained by mixing H₂O₂ (in ethanol/water (1.76:1, v/v) and bicarbonate through a three-way piece. The flow system used in this work was shown in Figure 1. It consists of a peristaltic pump with two lines. The flow streams H₂O₂ in 1.76:1 ethanol/water solution and bicarbonate were used to prepare the on-line HCO₃⁻ ions. The CL emission intensity was used to quantify HCO₃⁻ ions. Catalysis by sodium bicarbonate, potassium bicarbonate, and ammonium bicarbonate was carefully studied in ethanol/water, and the source of bicarbonate had a significant effect on the CL intensity. It was shown that ammonium bicarbonate was the best catalyst. The concentration of NH₄HCO₃ was optimized over the range of 0–0.2 mol/L in a FIA-CL mode described in the Experimental Section. The results showed that the CL intensity increased along with the increased concentration of NH₄HCO₃. However, if the concentration of NH₄HCO₃ was more than 0.05 mol/L, the CL intensity increased instead, and high concentrations of bicarbonate easily aroused solubility saturation effects. Thus, 0.05 mol/L ammonium bicarbonate was selected as the optimum concentration of NH₄HCO₃ throughout the study.

Second, the concentration of H₂O₂ optimized over the range 0–2 mol/L in ethanol/water (1.76:1, v/v) was examined.
Excessively high H$_2$O$_2$ concentration can give rise to air bubbles in the flow line. Excessively low H$_2$O$_2$ concentration cannot produce enough HCO$_4^-$ ions. So, after a series of experiments, 2 mol/L H$_2$O$_2$ was selected as the optimum.

Third, the mixing time interval and the flow rates of H$_2$O$_2$ and bicarbonate played key roles in the on-line preparation of HCO$_4^-$ solution. Both too-long and too-short times cannot support formation of enough HCO$_4^-$ ions to induce CL emission. In addition, the lifetime of the active carbon oxygen intermediate was a dominant factor in the flow CL system because transient light emission was monitored. Since the lifetime of the HCO$_3^-$ ions was very short, the point of mixing was reasonably designed. The experiments of the different mixing coil length and the effect of flow rates showed that when a 35 cm mixing coil and 1.1 mL/min flow rate were used, the maximum amount of HCO$_4^-$ ions were obtained. A mixing coil that is either too long or too short could not produce the most HCO$_4^-$ ions.

To examine the HCO$_4^-$ ions of on-line preparation, we used 98% $^{13}$C-enriched NaHCO$_3$ to examine bicarbonate—peroxide in ethanol/water solvents by $^{13}$C NMR at 25 °C. Hydrogen peroxide concentration of 2.0 mol/L was employed, and [H$^{13}$CO$_3^-$] = 0.05 mol/L for all studies. Ethanol/water (1.76:1, v/v) solutions of hydrogen peroxide with bicarbonate catalyst were mixed 10 min prior to the experiment to ensure the preequilibration of peroxymonocarbonate formation. Ethanol/water (1.76:1, v/v) solutions of hydrogen peroxide with bicarbonate catalyst were mixed 10 min prior to the experiment to ensure the preequilibration of peroxymonocarbonate formation. Since the peat for bicarbonate at 159.8 ppm, a single additional peak at 158.2 ppm assigned to HCO$_3^-$ was observed (chemical shifts relative to TMS). The peaks assigned to HCO$_3^-$, HCO$_4^-$, and EtOCO$_2^-$ in ethanol/water solution are shown in Figure 2. It was shown that the quantity of HCO$_3^-$ with the time change remained nearly steady within 20 min. Thus, on-line preparation of HCO$_3^-$ ions provided a reliable intermediate for further investigation.

3.2. The Energy Transfer CL Reaction in the Peroxymonocarbonate System. As one of the rare earth elements, complexes of europium (II) ion have received much attention due to its unique luminescence properties, such as long luminescence decay time and narrow emission bands which can form highly luminescent complexes with several groups of ligands. Of particular concern to its applications is the study of coordination compounds in solution and luminescent assays for biochemistry. After many experiments, the Eu(II)–dipicolinate complex was employed to investigate the energy transfer mechanism for the HCO$_4^-$ system. As shown in Figure 3, it was found that, by injecting Eu(III) (50 μL) into HCO$_4^-$ solution, CL emission was observed with our apparatus. However, when a Eu(II) solution (50 μL) was injected into HCO$_4^-$ solution, bright CL can be observed. When injecting Eu(II)–dipicolinate complex (50 μL) into HCO$_4^-$ solution, the CL was enhanced greatly. At the same conditions, when the Eu(II)–dipicolinate complex (50 μL) was also injected into H$_2$O$_2$ solution, no CL was observed. This sufficiently showed that HCO$_3^-$ played a key role as an oxidant rather than H$_2$O$_2$ in the system. Because the metal ions can induce CL emission, it was suspected that the Zn$^{2+}$ and its byproducts induced CL emission during the reduction process of Eu$^{3+}$ to Eu$^{2+}$. Therefore, the effects of Zn$^{2+}$ and its byproducts on the system were also investigated. When injecting Zn$^{2+}$ and its byproducts into the on-line preparation HCO$_3^-$ solution, no CL was observed. This sufficiently showed that the HCO$_3^-$–Eu(II)–dipicolinate system induced CL emission. The kinetic profiles of CL for the system HCO$_3^-$–Eu(II)–dipicolinate were shown in Figure 4, from which it was evident that a maximum was reached within several seconds when the Eu(II)–dipicolinate complex (50 μL) was also injected into HCO$_3^-$ solution. The
intensity of emission of lanthanide ions depended on the stability of the complex formed with the ligand and the La(III) hydration number.25,26 Experiments showed that the CL emission reached a maximum when the molar ratio of Eu(II) to dipicolinate was 1:1. The strong CL phenomenon provided the favorable condition for the mechanism study of the HCO$_4^-$-CL phenomenon.

The optimum conditions for the HCO$_4^-$-Eu(II)-dipicolinate reaction were investigated in detail, containing the effects of the molar ratio of ligand/metal, the flow rate, and sample volume on the CL intensity.

3.3. Investigation of the Mechanism in the HCO$_4^-$-Eu(II)-Dipicolinate Reaction. In the present work, we employed the equilibrium of bicarbonate-peroxide to form on-line HCO$_4^-$ ions. Many investigations have indicated that some of the lanthanide ions (mainly Eu(II)) showing strong luminescence were used as luminescent probes, activators, and energy transfers (donors or acceptors). HCO$_4^-$, as an active carbon oxygen intermediate, had high activity, and it was easy to oxidize Eu(II) to Eu(III). The CL spectral distribution was measured with the cutoff filter method, as shown in Figure 6. The strong maximum at about 620 nm indicated that the observed CL was emitted by the Eu$^{3+}$ ions. The $E^*$ value was 1.81 V for HCO$_3^-$/HCO$_4^-$ and $-0.43$ V for Eu$^{3+}$/Eu$^{2+}$.28 Taking into account the CL spectrum as well as the electrode potential of redox, we could conclude that the excitation of Eu$^{3+}$ to the luminescent level $^5D_{0}$ (2.10 eV) was possible. In the redox system of Ru$^{2+}$/Ru$^{3+}$ with 2,2'-bipyridine, the excited product was identified as a metal (Ru$^{3+}$) to ligand charge-transfer triplet.29 In addition to these, Elbanowsli et al.30 has found that the (Eu(II)-N$_3$)$_2^{2+}$ complex can easily accept energy from the singlet oxygen dimers. So, we deduced that HCO$_4^-$ ions could oxidize Eu(II) to Eu(III), and in this process, singlet oxygen was produced, which transferred its radical energy to the Eu(III).

The thermodynamic analysis estimates suggested the O-O bond homolysis as the activation step$^{31}$ during the process of oxidation for Eu(II). Simultaneously, the process brought the CO$_4^{2-}$ radical and the hydroxide radical. Radical recombination involved the perhydroxyl radical which transferred to the superoxide ion radical.

$$\text{H}_2\text{O}_2 + \text{CO}_3^{2-} \rightarrow \text{HCO}_3^- + \cdot\text{HO}_2^{32}$$

$$\cdot\text{HO}_2 \rightarrow \text{H}^+ + \text{O}_2^{33}$$

Reaction 4 was only the first step, which was followed by the interaction of perhydroxyl radical with superoxide ions and the interaction of two perhydroxyl radicals.34 The oxygen ion radical thus formed can take part in the following subsequent reactions leading to the formation of singlet oxygen molecules:

$$\text{O}_2^{*} + \cdot\text{OH} \rightarrow \text{O}_2 + \text{HO}^-$$

$$\text{HO}_2^* + \text{O}_2^{*} \rightarrow \text{O}_2 + \text{HO}_2^-$$

$$\text{HO}_2^* + \text{HO}_2^* \rightarrow \text{O}_2 + \text{H}_2\text{O}_2$$

Excess of H$_2$O$_2$ resulted in an increased yield of O$_2^{*}$, as well as the formation of singlet oxygen. The presence of singlet oxygen (O$_2^*$) was also studied using various methods, such as enhancing and quenching CL method as follows.

It is well-known that the luminescent reagents, such as luminol,35 lucigenin,36 and p-methoxyphenyl cypridina luciferin analogue (MCLA),37 can react with reactive oxygen species to generate bright CL emission. In particular, MCLA has been used as a CL probe for the determination of O$_2^*$ and O$_2$. Furthermore, it has been shown that other reactive oxygen species such as H$_2$O$_2$ and HO$^*$ are not able to elicit the luciferin analogue CL emission.38 Thus, the effect of the luminescent reagents on the HCO$_4^-$-system CL was investigated. At the same concentration (1 $\times$ 10$^{-5}$ mol/L), it was seen that these luminescent reagents enhanced greatly the CL intensity, and MCLA enhanced CL intensity 75 times, lucigenin about 30 times, and luminol 20 times. These showed that the O$_2^*$ was generated in this CL system. The generation of O$_2^*$ in the examined system was also confirmed by the observed quenching effect.39 The CL signal intensity was effectively quenched (about...
13 times) by NaN₃, which was a strong indication that ¹O₂ was the emitter. On the basis of these experiments data, we further speculated that ¹O₂ participates in the energy-transfer CL reaction. To further characterize the generation of ¹O₂ in this CL reaction, the ESR spin-trapping technique and mass spectra were explored.

Room-temperature ESR spectroscopy was used to detect and identify free radical intermediates formed during reactions. Since some of the free radicals in these experiments were too short-lived to be detected directly, the spin-trapping technique was used. 2,2,6,6-Tetramethylpiperidone (TEMP)-specific target molecule of ¹O₂, was used as the spin-trapping reagent. The reaction of ¹O₂ with TEMP results in the formation of 2,2,6,6-tetramethylpiperidone-N-oxide (TEMPO), and a product being a stable nitroxide radical with a characteristic spectrum. Reagents were dissolved in appropriate amounts in alcohol. The choice of alcohol as a cosolvent was supported by several arguments: TEMP was soluble in alcohols, the lifetime of ¹O₂ was increased six times in comparison to H₂O, and an interaction of ·OH with TEMPO was suppressed. The sample in a flat quartz cell was measured in the cavity of the ESR spectrometer. No signal was detected in the TEMP background. The original free radical intermediate was then identified by the resulting hyperfine coupling constants of its TEMP adduct. ESR spectra were recorded with a Bruker ESP-300E spectrometer operating in the X-band at room temperature. The microwave frequency was 9.83 GHz, and the modulation amplitude was 2.035 G.

Spectra were recorded on a computer interfaced to the spectrometer. Figure 7 presented the production of ¹O₂ in the reaction of HCO₄⁻—Eu(II)—dipicolinate system.

To chemically detect ¹O₂, we used 9,10-diphenylanthracene (DPA), which was suitable for reactions in organic phases. This method was based on the rapid and specific reaction of ¹O₂ with DPA (k = 1.3 × 10⁹ M⁻¹ s⁻¹) forming a stable DPA endoperoxide (DPAO₂). After the reaction, the solution was diluted 1:100. DPA and its endoperoxide (DPAO₂) were analyzed by electrospray ionization mass spectrometry analyses. Full-scan data were acquired over a mass range 100–500 m/z. The mass spectrum of DPA recorded in the positive mode exhibits a major [M]+ ion at m/z = 330, corresponding to the positively charged molecular ion. The spectrum of DPAO₂ displayed an intense [M + H]+ ion at m/z = 363. The reaction of HCO₄⁻ and Eu(II) in the presence of 60 mM DPA resulted in the formation of DPAO₂. Detection of the anthracene endoperoxide (DPAO₂) provided further evidence of the formation of ¹O₂ in this HCO₄⁻—Eu(II)—dipicolinate CL system (Figure 8). For the sake of comparison, we also detected the ¹O₂ deriving from the H₂O₂/molybdate and H₂O₂/hypochlorite systems by mass spectrometry. Their results were coincident. These novel observations identified the generation of ¹O₂ in the reaction of HCO₄⁻ with Eu(II)/Eu(III)—dipicolinate complex, suggesting a potential ¹O₂-dependent mechanism.

According to the literature, it can be concluded that ¹O₂ generated during the reaction included O₂ (¹Δg) and O₂ (³Σg⁺), being of higher energy than the ground-state triplet oxygen, which can transfer its excess energy to acceptor (Eu(II/III)—dipic), thereby engendering CL emission.

\[
O_2 (¹Δg) + O_2 (¹Δg) \rightarrow O_2 (³Σg⁺) + O_2 (³Σg⁻) \quad K = 1.3 \times 10^3 \quad (8)
\]

\[
O_2 (³Σg⁺) + O_2 (¹Δg) + [Eu(III)(dipic)]^- \rightarrow 2O_2 (³Σg⁺) + [Eu(III)(dipic)*]^− \quad (9)
\]

The product of Eu(II) ion oxidized by peroxymonocarbonate is Eu(III) ions. The Eu(III)—dipicolinate complex accepted energy from the singlet oxygen to obtain the excited Eu(III)—dipicolinate complex which, on returning to the ground state, emits radiation of wavelength λ = 615 nm corresponding to the transition ⁵D₀→⁷F₂.¹⁶

\[
[Eu(III)(dipic)*]^− \rightarrow [Eu(III)*(dipic)]^- \quad (10)
\]

\[
[Eu(III)*(dipic)]^- \rightarrow [Eu(III)(dipic)]^- + hν \quad (11)
\]

Besides the dominant band at λ = 615 nm, the CL spectra include a low-intensity band with a maximum at about 490 nm, which can be interpreted as arising from the emission of excited carbonyl groups.⁴⁰,⁴⁷

4. Conclusions

A simple, rapid, and convenient method to prepare peroxymonocarbonate ions based on the continuous flowing stream was developed. The kinetic and spectroscopic results strongly supported the formation of peroxymonocarbonate ions. The reaction of hydrogen peroxide and bicarbonate to form peroxymonocarbonate proceeded rapidly near neutral pH in ethanol/water mixtures. Solubility of the bicarbonate catalyst was enhanced by use of NH₄HCO₃ rather than group I salts, which tended to have low solubility in the mixed solvents and could lead to phase separation.
A high electrode potential for the HCO₃⁻/H₂CO₃⁻ couple (1.8 ± 0.1 V vs NHE) can induce an ultraweak chemiluminescence in the HCO₃⁻—Eu(II) system. When adding dipicolinate into this system, the chemiluminescent emission intensity was efficiently enhanced. The CL mechanism of HCO₃⁻—Eu(II)—dipicolinate system was investigated in detail by various methods. Briefly, the peroxymonocarbonate oxidation system was an inexpensive and relatively nontoxic alternative to other oxidants, and our experiments indicated that it can be used in the systems where a mild, neutral pH was required. The potential role peroxymonocarbonate ions as a reactive oxygen species is worthy of further investigation in view of the kinetic and mechanistic results. Further studies of this type are underway in our laboratory.

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