Experimental Studies on the Chemiluminescence Reaction Mechanism of Carbonate/Bicarbonate and Hydrogen Peroxide in the Presence of Cobalt(II)

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Chemiluminescence (CL) phenomena of carbonates or bicarbonates of potassium, sodium, or ammonium with hydrogen peroxide in the presence of cobalt sulfate were reported. After cobalt(II) solution was injected into the mixture of carbonate/bicarbonate and hydrogen peroxide, a CL signal was given out briefly. The CL conditions of these systems were optimized. The CL reaction mechanisms were studied experimentally by examining the spectrum emitted by the CL system and the effect of various free radical scavengers on CL emission intensity. The results showed that the maximal emission wavelengths of the $CO_3^{2-}-H_2O_2-Co^{2+}$ and $HCO_3^{-}-H_2O_2-Co^{2+}$ systems were 440 and 490 nm, respectively. As a result, a radical scavenger of ascorbic acid, thiourea, and superoxide dismutase exhibited different effects on these CL systems. The different CL mechanisms involving the carbon dioxide dimer and the oxygen dimer were revealed, respectively.

1. Introduction

Analytical methods based on chemiluminescence (CL) have made many chemists interested in this field because of a triumvirate of inherent strengths: sensitivity, simplicity, and, in many cases, a wide linear detection range. They have taken a strong position among the more mundane analytical techniques during the last 40 years.[1] Chemiluminescent reactions are mostly based on the oxidation of luminescent reagents such as luminol, lucigenin, and so on by a highly oxidized species, in which peroxides are prevalent because the relatively weak peroxide bond is easily cleaved and the resulting molecular reorganization liberates a large amount of energy. Hydrogen peroxide is a widely used oxidant with high active oxygen content, but H_2O_2 is a rather slow oxidizing agent in the absence of activators.[2,3] Common activators include transition metals and their compounds (usually Fe^{2+}), manganese dioxide, potassium permanganate, and enzyme. And through catalysis, H_2O_2 can be catalytically broken down into hydroxyl radicals ($^{\bullet}OH$). Therefore, CL emission from the catalytic decomposition of hydrogen peroxide (H_2O_2) has been recognized for a long time, and many CL interrelated systems have been reported.[11−14] These chemiluminescent systems containing luminescent reagents face the shortcoming of selectivity. The CL phenomena through the decomposition of H_2O_2 without any special CL reagents is an interesting underinvestigated field, which hitherto few investigated.

A novel method for activating H_2O_2 by using bicarbonate ion was described by Drago and co-workers in their study on the oxidation of chemical warfare agents and simulant sulfides in 1998.[8] Research efforts on the activation mechanism revealed the process via formation of a peroxymonocarbonate ion, HCO_4^-, a previously unrecognized reactive oxygen species.[9−13] Peroxycarboxylic acid has become a favored method in large-scale bleaching applications and many synthetic oxidations,[14,15] but it seldom was used for analytical purposes. To the best of our knowledge, the CL systems concerning H_2O_2, carbonate or bicarbonate, and transition metal ions without special CL reagents are reported in the following literature. Liu et al. reported the CL of 2.0 mol/L H_2O_2 and 0.05 mol/L NH_4HCO_3 in the presence of Eu(II) in the cosolvent of ethanol and water and revealed the mechanism of CL originating from singlet oxygen via energy transfer chemiluminescence.[16] Zhang and his co-workers found the chemiluminescence of $Co^{2+}-H_2O_2-HCO_3^-$, and the CL intensity could be significantly enhanced when rhodamine B coexisted. They thought that the CL was produced by excited double oxygen $(O_4)^*$.[17] At a later time, they reported the enhanced chemiluminescence from the reaction of hemoglobin (Hb) with hydrogen peroxide in an aqueous carbonate solution in the medium of 0.01 M NaOH by β-cyclodextrin (β-CD), but not enough experimental data proved the mechanism.[18] Staninski et al. studied the kinetic curves and CL emission spectrum of the system of $Eu(II)-H_2O_2-HCO_3^-$.[19] Excited Eu^{3+} ions and excited products of carbonate decomposition were thought to be the emitters on the basis of the characteristic bands in the CL spectrum.

In this work, the different chemiluminescent phenomena of hydrogen peroxide with carbonate or bicarbonate of potassium, sodium, and ammonium in the presence of Co^{2+} were investigated systemically. The proposed CL systems have superior sensitivity and simple reactions without any special luminescent reagents, buffer conditions, and other additives. In addition, the mechanism was discussed by examining the CL spectrum and the effect of various free radical scavengers on CL emission intensity.

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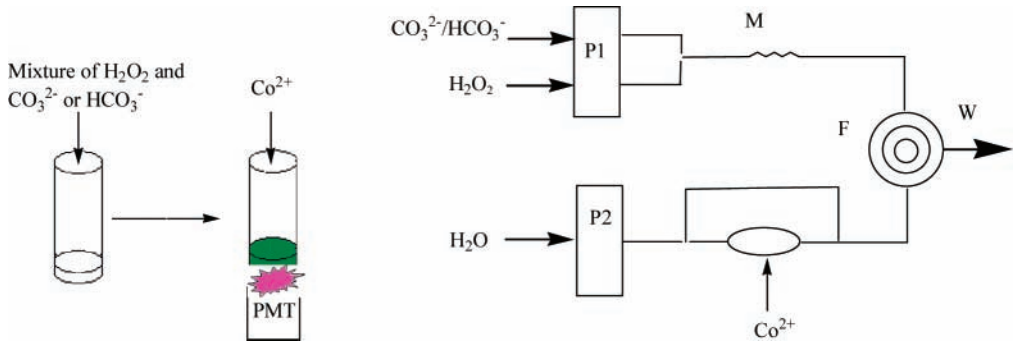
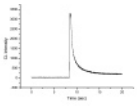
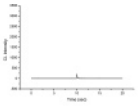
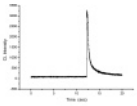
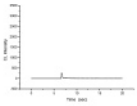
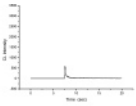
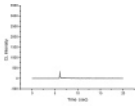


Figure 1. Manifold used for chemiluminescent detection systems: (a) batch method; (b) flow-injection method. P1 and P2, peristaltic pump; M, mixed pipe; F, CL cell; W, wastewater.

TABLE 1: Chemiluminescent Profiles and Intensities of Different Carbonates or Bicarbonates[a]

profiles						
intensity	3301	276	3219	328	762	299

[a] CL profiles when 25 μL of 1.0 mol/L of CO_3^{2-} or HCO_3^- was mixed with 25 μL of 0.2 mol/L of H_2O_2, then 50 μL of Co^{2+} was injected.

2. Experimental Section

2.1. Chemicals and Solutions. All chemicals were of analytical grade and used without further purification. All solutions were prepared using 18.3 MΩ water obtained from a Milli-Q purification system (Barnstead Thermoyne).

Solutions of 1.0 mol/L carbonate and bicarbonate and 0.01 mol/L cobalt sulfate were prepared by dissolving the corresponding solute in pure water. H_2O_2 was diluted to 0.2 mol/L by pure water from 30% (w/w) solution. In the CL determination, they were diluted to the required concentration. NH_4HCO_3 and H_2O_2 were prepared daily.

2.2. Instrumentation. The batch method was carried out with an UPCL ultraweak chemiluminescence analyzer (Institute of biophysics, Chinese Academy of Science, Beijing, China) using a 3 mL glass cuvette. The signal was recorded by a computer equipped with a data-acquisition interface. Data acquisition and treatment were performed with BPCL software. The flow-injection chemiluminescent signal was measured with a model LF-800 flow-injection system (Microtec NITI-On, Funabashi, Japan).

The spectrophotometric investigation was performed in 1 cm quartz optical cells with a UV-2401PC (Shimazu, Japan) spectrometer. The emission spectrum was measured on a model FL-2500 spectrofluorometer (Hitachi, Japan) when the Xe lamp was turned off.

2.3. Procedure. Light-producing reactions were carried out in the cuvette, and the CL profile and intensity were displayed and integrated for a 0.01 s interval. As shown in Figure 1, a 50 μL mixture of H_2O_2 and CO_3^{2-} or HCO_3 (1:1 v/v) and a 50 μL fluorescent agent were added to the cuvette by an adjustable volume mechanical pipette, then 50 μL of Co^{2+} was injected by a microliter syringe from the upper injection port.

In the flow-injection chemiluminescence determination, 50 μL of Co^{2+} was injected into the carrier stream through the injector and mixed with the H_2O_2 and CO_3^{2-} or HCO_3^- mixture through a three-way piece. The signals were recorded with a PC. A schematic diagram is shown in Figure 1.

3. Results and Discussion

3.1. Comparison of Chemiluminescent Signals of Different Carbonates or Bicarbonates in the Presence of H_2O_2 and Co^{2+}. Carbonates or bicarbonates of potassium, sodium, and ammonium were mixed with hydrogen peroxide separately in same volume. After the injection of Co^{2+}, the chemicals reacted momentarily. During the chemical reaction, the CL signals were measured according to the method described above. Time courses of the kinetic profiles and intensities of the chemiluminescent reaction are shown in Table 1.

From Table 1, the following results could be deduced:

(1) The CL intensity of carbonate is stronger markedly than that of bicarbonate.

(2) The CL intensity of the three kinds of cation is in the order of potassium ≈ sodium > ammonium.

In the following measurements, different fluorescent (FL) agents, namely, Eosin Y, dichlorofluorescein (DCF), and Rhodamine B (RhB) were added to the $Co^{2+}-NH_4HCO_3-H_2O_2$ chemiluminescent system, respectively. The results in Figure 2 showed that the chemiluminescent system of $Co^{2+}-NH_4HCO_3-H_2O_2$ only emitted a weak CL, but the CL intensity could be enhanced obviously by fluorescent reagents. The enhanced CL provided a potential application for the $Co^{2+}-NH_4HCO_3-H_2O_2$ system.

The chemiluminecent systems of direct CL of $K_2CO_3/Na_2CO_3-H_2O_2-Co^{2+}$ and enhanced $NH_4HCO_3-H_2O_2-Co^{2+}$ by fluorescent agent were optimized in the following experiment. The proposed CL signals also were measured by a flow-injection chemiluminescent system shown in Figure 1, and sharp peaks could be obtained.

3.2. Chemiluminescence of Different Metal Ions. Different transition metal ions in low-valence compounds were injected to the mixture of H_2O_2 and CO_3^{2-} or HCO_3^-, and the CL intensities were determined, respectively. The results are shown in Table 2. The CL intensities of these ions were $Co^{2+} \approx Fe^{2+} > Ni^{2+} \approx Cu(I) > Mn^{2+}$.

3.3. Effects of the Concentrations of Chemicals. A series of experiments were conducted to establish optimum analytical

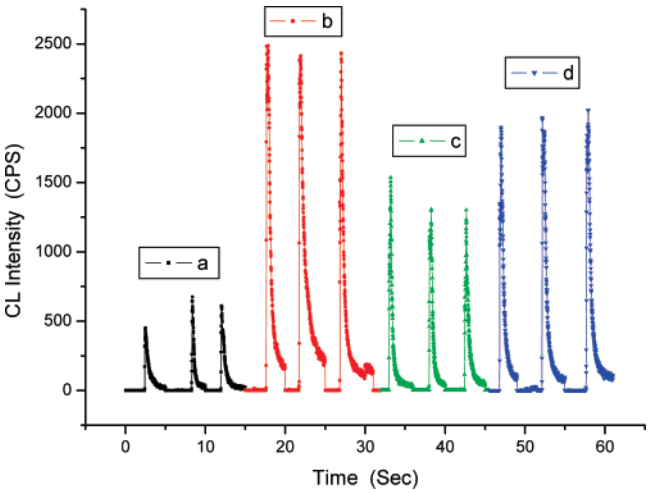


Figure 2. CL profiles of $NH_4HCO_3-H_2O_2-Co^{2+}$: (a) H_2O; (b) 10^{-5} mol/L Eosin Y; (c) 10^{-5} mol/L rhodamine B; (d) 10^{-5} mol/L dichlorofluorescein. CL conditions: $C_{NH_4HCO_3} = 1.0$ mol/L, $C_{H_2O_2} = 0.2$ mol/L, $C_{CoSO_4} = 0.01$ mol/L.

TABLE 2: CL Intensities of Different Transition Metal Ions[a]

	K_2CO_3	$KHCO_3$	Na_2CO_3	$NaHCO_3$	$(NH_4)_2CO_3$	NH_4HCO_3
$CoSO_4$	3301	276	3216	328	762	299
$FeSO_4$	3302	453	3316	508	2395	137
$Ni(NO_3)_2$	559	29.4	367	20	41	*b*
CuCl	610	16	958	16		
$MnSO_4$	23		26			

[a] CL profiles when 25 μL of 1.0 mol/L of CO_3^{2-} or HCO_3^- was mixed with 25 μL of 0.2 mol/L of H_2O_2, then 50 μL of metal compounds was injected, respectively (except CuCl, which was injected as a saturated solution). [b] No CL signal was emitted.

variables and deduce the reaction mechanism. The effect of the concentrations of chemicals was tested first.

Approximately 0.01 mol/L $CoCl_2$, $CoSO_4$, $Co(NO_3)_2$, and $Co(Ac)_2$ were added, respectively, to the mixture of $CO_3^{2-}-H_2O_2$ or $HCO_3^--H_2O_2$. The results showed no remarkable difference among these cobalt compounds. $CoSO_4$ was used in the following CL studies. The effect of the concentration of $CoSO_4$ on the CL intensity was tested further, and the results are shown in Figure 3a. These results revealed the fact that Co^{2+} was the limiting reactant. Approximately 0.01 mol/L Co^{2+} was selected in the subsequent research.

The effect of H_2O_2 concentration from 0 to 2.0 mol/L was tested. The results are shown in Figure 3b. The signals were enhanced obviously with the increase of H_2O_2, but too concentrated H_2O_2 reduced the signals.

In the $CO_3^{2-}-H_2O_2-Co^{2+}$ system, different concentrations of Na_2CO_3 from 0 to 1.0 mol/L were mixed with 0.02 mol/L H_2O_2, and the CL signals were measured, respectively. The results are shown in Figure 3c. Na_2CO_3 in the range of 0.65−1.0 mol/L could produce high and stable signals. Na_2CO_3 was difficult to dissolve completely when its concentration exceeded 1.0 mol/L. In the $HCO_3^--H_2O_2-Co^{2+}$ system, the influence of the NH_4HCO_3 concentration on the emission intensity was shown in Figure 3c. The CL intensity enhanced with the increase of the NH_4HCO_3 concentration in the range of 0.1−1.0 mol/L and reached a plateau at a higher concentration.

3.4. Elementary Investigation of the CL Reaction by UV−Vis Spectroscopic Methods. To investigate the reaction among carbonate/bicarbonate, H_2O_2 and cobalt, UV−vis spectrometric methods were employed to the systems of $Co^{2+}-H_2O_2-NH_4HCO_3$ and $Co^{2+}-H_2O_2-NH_4HCO_3$−Eosin Y. The spectra are

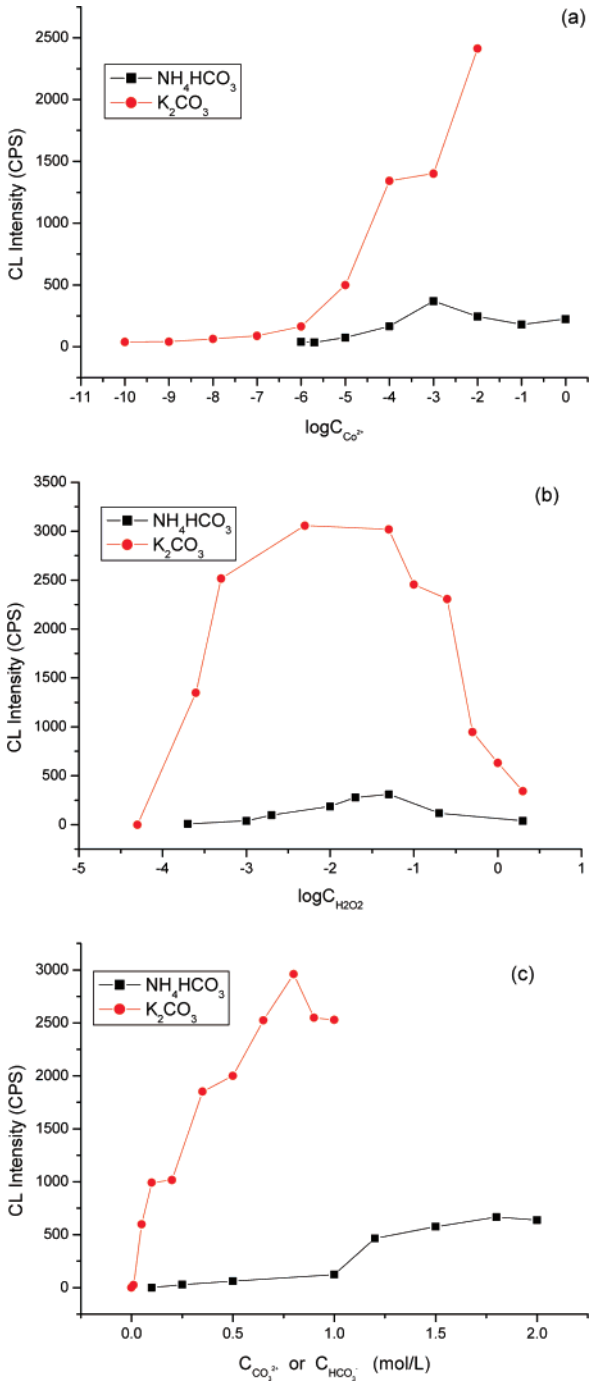


Figure 3. Effect of reagent concentrations on the CL signals: (a) Co(II); (b) H_2O_2; (c) CO_3^{2-}/HCO_3^-. Conditions: (a) $C_{Na_2CO_3} = 1.0$ mol/L, $C_{NH_4HCO_3} = 1.0$ mol/L, $C_{H_2O_2} = 0.2$ mol/L; (b) $C_{Na_2CO_3} = 1.0$ mol/L, $C_{NH_4HCO_3} = 1.0$ mol/L, $C_{CoSO_4} = 0.01$ mol/L; (c) $C_{CoSO_4} = 0.01$ mol/L, $C_{H_2O_2} = 0.2$ mol/L.

shown in Figure 4. The curves c and e in Figure 4 suggested a green result was produced with $\lambda_{max} = 590.00$ nm. This result was a compound containing cobalt and could change gradually into blue after several hours and λ_{max} shifted to 580.50 nm. This fact indicated that Co^{2+} participates in the redox reaction. Hence, Co^{2+} reacted with H_2O_2, apparently with the formation of Co(III). The generally accepted mechanism of CL reactions in the presence of Co^{2+} was Co^{2+} acting as a catalyst.[1,20−25] On the basis of this experiment, the reactions of $Co^{2+} + CO_3^{2-}-H_2O_2$ and $Co^{2+} + HCO_3^--H_2O_2$ show a different route from the universally accepted catalysis of Co^{2+}.

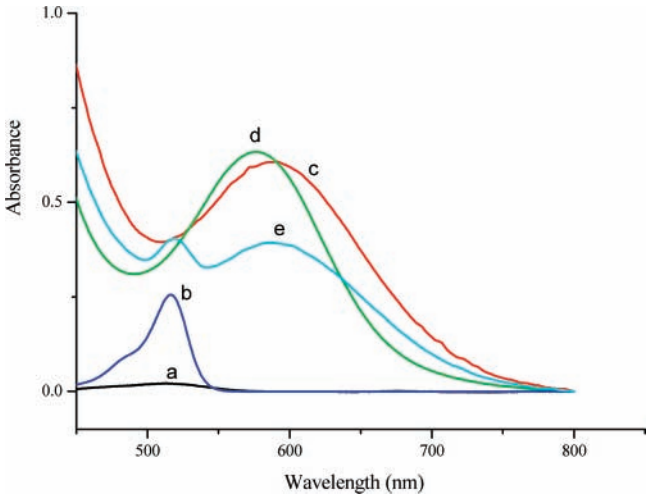


Figure 4. Spectra of proposed CL reactants and products: (a) 10^{-2} mol/L Co^{2+}; (b) 3.3×10^{-6} mol/L Eosin Y; (c) 10^{-2} mol/L Co^{2+} + 0.2 mol/L H_2O_2 + 0.5 mol/L NH_4HCO_3; (d) reaction c after 12 h; (e) 10^{-5} mol/L Eosin Y + reaction c.

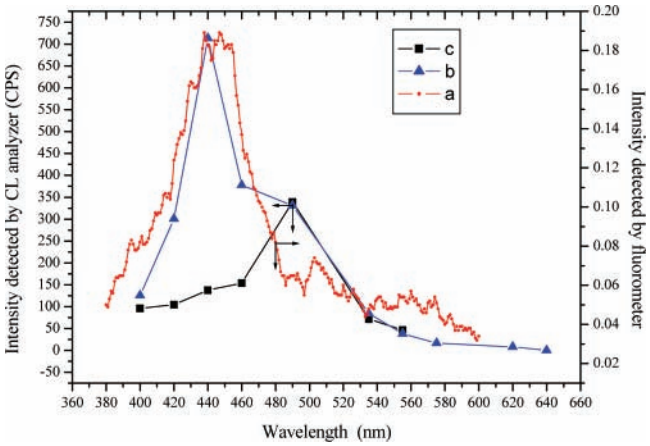


Figure 5. Emission spectra of $CO_3^{2-}-H_2O_2-Co^{2+}$ and $Co^{2+}-H_2O_2-HCO_3^-$. (a) $CO_3^{2-}-H_2O_2-Co^{2+}$ spectrum measured by fluorescence spectrometer. CL conditions: $C_{K_2CO_3} = 1.0$ mol/L, $C_{H_2O_2} = 0.2$ mol/L, $C_{CoSO_4} = 0.1$ mol/L. (b) $CO_3^{2-}-H_2O_2-Co^{2+}$ spectrum measured by luminometer. CL conditions: $C_{Na_2CO_3} = 1.0$ mol/L, $C_{H_2O_2} = 0.2$ mol/L, $C_{CoSO_4} = 0.01$ mol/L. (c) $Co^{2+}-H_2O_2-HCO_3^-$ spectrum measured by luminometer. CL conditions: $C_{NaHCO_3} = 1.0$ mol/L, $C_{H_2O_2} = 0.2$ mol/L, $C_{CoSO_4} = 0.01$ mol/L.

3.5. Emission Spectrum of CL Systems. To identify the emitting species in the $Co^{2+}-H_2O_2-CO_3^{2-}$ CL system, the CL spectra were measured with a fluorescence spectrometer and luminometer, respectively. Approximately 1.0 mol/L K_2CO_3, 0.2 mol/L H_2O_2, and 0.1 mol/L $CoSO_4$ were pumped through separate lines into a cell placed inside the cell holder of the fluorescence spectrophotometer. The flow rates of the solutions were 4.0 mL/min. The excitation Xe lamp was turned off, and the emission slit width was opened maximally to 20 nm during the recording of the CL spectrum. The CL spectrum measured by fluorescence spectrometric methods is shown in Figure 5a. The CL spectrum information was achieved also using 10 narrow band interference filters (400−640 nm), which were inserted between the cuvette and the photomultiplier tube. The CL signals were recorded at different wavelengths ($C_{Na_2CO_3} =$ 1.0 mol/L, $C_{H_2O_2} = 0.2$ mol/L, $C_{CoSO_4} = 0.01$ mol/L). The CL spectrum obtained by this method is shown in Figure 5b. It could be seen that the maximum of the CL spectrum was located at 440 nm.

The chemiluminescent emission spectrum of $Co^{2+}-H_2O_2-HCO_3^-$ was measured using 10 narrow band interference filters only, because the chemiluminescent signal was not high enough to be detected by a refitted fluorometer as the $Co^{2+}-H_2O_2-CO_3^{2-}$ system. The results are shown in Figure 5c. The CL of the $Co^{2+}-HCO_3^--H_2O_2$ system has shown one predominant emitter at 490 nm.

3.6. Effects of Different Radical Scavengers on the CL System. In the system containing metals at different degrees of oxidation, the introduction of hydrogen peroxide initiates a number of reactions, mainly of the radical type.[19] To obtain further insight into the mechanism of the CL systems, the effects of various active oxygen radical scavengers on the CL emission intensity were investigated. Approximately 20 μL of radical scavengers of different concentrations was added to the CL systems, respectively, and the CL intensity was recorded. The percentage of CL inhibition was calculated as $\Delta I/I_0 \times 100\%$, and $\Delta I = I_0 - I$, where I and I_0 were the CL intensities of the $CO_3^{2-}/HCO_3^--H_2O_2-Co^{2+}$ system with and without radical scavengers, respectively. Another parameter, IC_{50}, which is the concentration with the percent inhibition equal to 50%, also was indicated.

3.6.1. Effects of Ascorbic Acid. Ascorbic acid is a well-known common free radical scavenger. Approximately 20 μL of ascorbic acid of different concentrations was added to the CL system, and the results are shown in Figure 6a. Considerable quenching of the CL was observed at relatively low concentrations of ascorbic acid. These results further confirmed the radical reaction mechanism of the proposed two CL systems. The generation of free radicals appeared to be the critical controlling factors in the proposed CL reactions.

3.6.2. Inhibition Effects of Thiourea. Among the oxygen-centered free radicals, the hydroxyl radical ($^{\bullet}OH$) is considered to be one of the most potent oxidizers.[26] Thiourea is an effective radical scavenger for $^{\bullet}OH$.[27] The inhibited CL signals were measured, respectively, after the addition of 20 μL of thiourea at different concentrations. Figure 6b shows the experimental results. The percentage inhibition for thiourea increased with its concentration, but the thiourea IC_{50} of the $CO_3^{2-}-H_2O_2-Co^{2+}$ system was higher obviously than that of the $HCO_3^--H_2O_2-Co^{2+}$ system.

3.6.3. Inhibition Effects of Superoxide Dismutase. Superoxide dismutase (SOD) catalyzes the dismutation reaction of superoxide anion radicals ($O_2^{\bullet-}$) to give ground state molecular oxygen and H_2O_2.[28] Thus the addition of SOD to the CL systems may halt the CL signals by reacting with $O_2^{\bullet-}$. Deferent amounts of SOD were added to the CO_3^{2-} and HCO_3^- CL systems, respectively. The results in Figure 6c show the inhibition effect of SOD on the $HCO_3^--H_2O_2-Co^{2+}$ system, but SOD did not completely inhibit the light emission even at its high concentration. On the contrary, no inhibition effect was observed on the $CO_3^{2-}-H_2O_2 + Co^{2+}$ system. This result confirmed that no $O_2^{\bullet-}$ was involved in the $CO_3^{2-}-H_2O_2 + Co^{2+}$ CL process.

On the basis of this result, the $CO_3^{2-}-H_2O_2-Co^{2+}$ system showed different light-emitting mechanisms from $HCO_3^--H_2O_2-Co^{2+}$.

3.6.4. Effect of Sodium Azide (NaN_3). NaN_3, a scavenger for singlet oxygen ($^1O_2$), was added to the $HCO_3^--H_2O_2-Co^{2+}$ and $CO_3^{2-}-H_2O_2-Co^{2+}$ systems. No inhibition effect was shown, suggesting that no $^1O_2$ was involved in the CL reaction.

On the basis of the above radical scavenger experimental results, $^{\bullet}OH$ was one of the inter-resultants in a series reaction of the $CO_3^{2-}-H_2O_2-Co^{2+}$ system, while $O_2^{\bullet-}$ and $^{\bullet}OH$ were

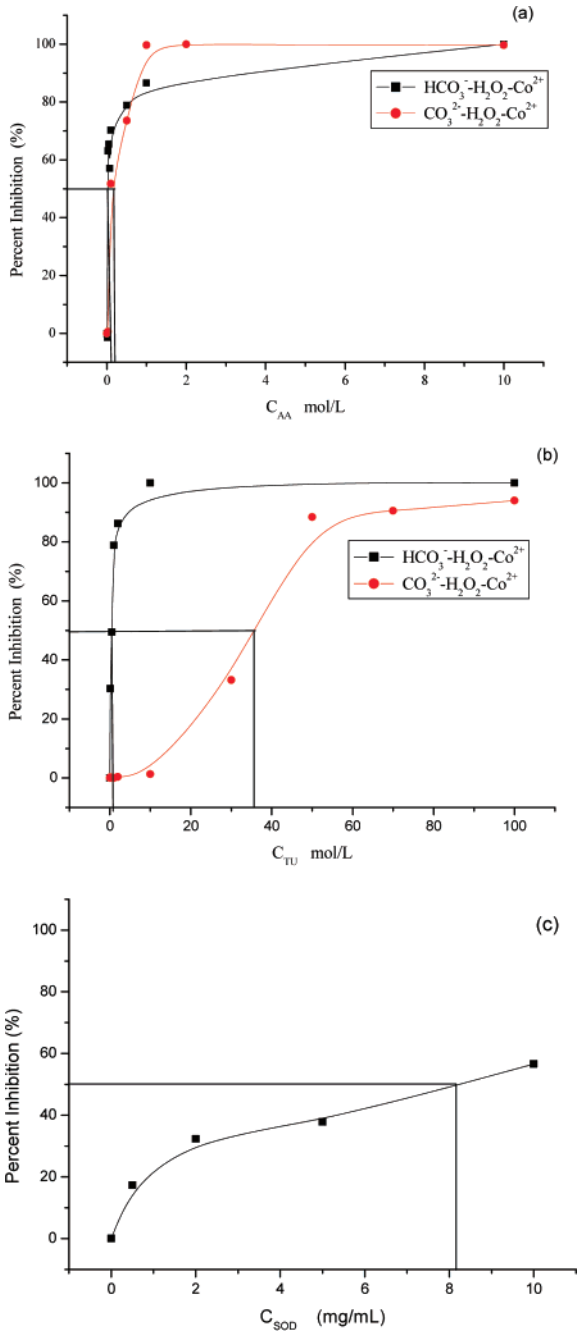


Figure 6. Effects of the radical scavengers of ascorbic acid, thiourea, and SOD. (a) $HCO_3^--H_2O_2-Co^{2+}$ system with ascorbic acid, IC_{50} = 0.05 mg/mL; (b) $CO_3^{2-}-H_2O_2-Co^{2+}$ system with ascorbic acid, IC_{50} = 0.2 mg/mL; (c) $HCO_3^--H_2O_2-Co^{2+}$ system with thiourea IC_{50} = 0.5 mmol/L; (d) $CO_3^{2-}-H_2O_2 + Co^{2+}$ system with thiourea, IC_{50} = 35 mmol/L; (e) $HCO_3^--H_2O_2-Co^{2+}$ system with SOD (IC_{50} = 8.2 mg/mL).

all involved in the $HCO_3^--H_2O_2-Co^{2+}$ system. $^1O_2$ was independent of these CL reactions.

3.7. Possible Mechanism of the CL System. On the basis of the above emission spectrum of CL, radical scavenger experimental results, and many reported studies, the possible CL mechanism of $CO_3^{2-}-H_2O_2-Co^{2+}$ deduced through $(CO_2)_2$* and the reaction process summarized in Scheme 1.

During the $CO_3^{2-}-H_2O_2-Co^{2+}$ CL process, the generation of $^{\bullet}OH$ by $H_2O_2-Co^{2+}$ (R1) was the initiative step. This has been proved by the addition of thiourea. Wu et al. also proved it by a new system of $H_2O_2-Co^{2+}$−bromopyrogallol red.[29] $^{\bullet}OH$ as a strong oxidant reacted with Co^{2+} was a fast step (R2).

SCHEME 1: Possible Mechanism for $CO_3^{2-}-H_2O_2-CO^{2+}$ Chemiluminescence Involving Carbon Dioxide Dimer

Dioxide Dimer

$Co^{2+} + H_2O_2 \rightarrow Co^{3+} + OH^- + {}^{\bullet}OH$ (R1)[29]

$Co^{2+} + {}^{\bullet}OH \rightarrow Co^{3+} + OH^-$ (R2)

$Co^{3+} + 3OH^- \rightarrow CoO(OH)\downarrow + H_2O$ (R3)

${}^{\bullet}OH + CO_3^{2-} \rightarrow CO_3^{\bullet-} + OH^-$ (R4)[30,31]

$2CO_3^{\bullet-} \rightarrow (CO_2)_2^* + O_2$ (R5)

$(CO_2)_2^* \rightarrow 2CO_2 + h\nu$ (λ= 430~450nm) (R6)[32,33]

SCHEME 2: Possible Mechanism for $HCO_3^--H_2O_2-Co^{2+}$ Chemiluminescence Involving Oxygen Dimer

Oxygen Dimmer

$Co^{2+} + H_2O_2 \rightarrow Co^{3+} + OH^- + {}^{\bullet}OH$ (R1)[29]

${}^{\bullet}OH + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O$ (R7)[34,35]

$HOO^{\bullet} \rightleftharpoons O_2^{\bullet-} + H^+$ (pKa=4.8) (R8)

$H^+ + HCO_3^- \rightarrow H_2O + CO_2$ (R9)

$2\ O_2^{\bullet-} + 2\ O_2^{\bullet-} + 4H_2O \rightarrow (O_2)_2^* + 2H_2O_2 + 4\ OH^-$ (R10)[37]

$(O_2)_2^* \rightarrow 2O_2 + h\nu$ (λ= 490~500nm) (R11)[32]

The resulting Co^{3+} was precipitated fast with the OH^- (R3), and this process altered the reaction of R1 and R2. The $^{\bullet}OH$ radical then reacted with CO_3^{2-} and gave free $^{\bullet}CO_3$ radical, resulting in the production of a carbon dioxide dimer (R4 and R5).[30,31] The CL band around 440 nm was ascribed from the energy release of excited $(CO_2)_2$ to the ground state.[32,33] These reaction processes are summarized in Scheme 1.

During the $HCO_3^--H_2O_2-Co^{2+}$ CL process, $^{\bullet}OH$ radical formed by $H_2O_2-Co^{2+}$ (R1) reacted with residual H_2O_2, giving $HO_2^{\bullet}$ (R7).[34,35] It is well-known that the hydroperoxyl radical is dependent upon the acid−base equilibrium.[36] In the mixed system of HCO_3^- and H_2O_2, H^+ reacted with HCO_3^- and released CO_2 gas (R9), which was proved by changing the clear limewater into a turbid solution. R9 broke the reaction equilibrium of R8, and this process accelerated the generation of $O_2^{\bullet-}$. Recombination of the $O_2^{\bullet-}$ radical caused the formation of oxygen dimer, which released the excited energy immediately, as a result, light near 490 nm emitting.[37] These reactions are shown in Scheme 2.

4. Conclusion

In this study, we showed six kinds of chemiluminescent systems without any expensive CL reagents. The CL emissions of carbonate and bicarbonate were observed in various spectrum regions. The inhibition of different radical scavengers contributed to the understanding of the CL mechanism. The mechanism of $HCO_3^--H_2O_2-Co^{2+}$ and $CO_3^{2-}-H_2O_2-Co^{2+}$ involving oxygen and carbon dioxide dimer was proposed, differing from the normally accepted mechanism of the luminol CL reaction with carbonate or bicarbonate as buffers. Research on the applications is in progress in our laboratory.

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