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Degradation of rhodamine 6G in the peroxyoxalate chemiluminescent reaction

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Abstract

The degradation process of rhodamine 6G in the peroxyoxalate chemiluminescent system was monitored for the first time. A preferential degradation of rhodamine 6G dimers was suggested and identified spectroscopically. The influence of light irradiation or H_2O_2 oxidation on dye degradation was insignificant according to our observations. The possible cause of rhodamine 6G degradation in the peroxyoxalate chemiluminescent system was discussed.

Keywords: Degradation; Rhodamine 6G; Peroxyoxalate; Chemiluminescence reaction

1. Introduction

Chemiluminescence can be defined as the emission of light by the generation of electronically excited states via a chemical reaction. The oxalate ester–hydrogen peroxide system exhibits high efficiency in this respect.

Although much is known about the peroxyoxalate chemiluminescent reaction, the reaction mechanism remains obscure, in particular, the presence of the key intermediate 1,2-dioxetanedione and the details of the energy transfer process occurring between the energy-rich species and the fluorescer [1–4].

In previous studies, a number of different classes of fluorescent dyes have been investigated in the peroxyoxalate chemiluminescent system, such as rhodamines, fluoresceins, benzoxazoles, anthracences and perylenes. An optimum fluorescer should have a high fluorescence efficiency, high excited state yield and high stability to hydrogen peroxide and photo-oxidation in the reaction [5]. However, to our knowledge, a detailed study of the degradation of fluorescers in the chemiluminescent reaction has not been published. Such information will be useful, not only in dye selection, but also in the elucidation of the chemiluminescent reaction mechanism.

In this study, we examine the degradation of rhodamine 6G (R6G) in the peroxyoxalate chemiluminescent system with a diode array spectrophotometer. The multichannel characteristics of this instrument enable us to obtain the entire UV–visible spectrum simultaneously. In addition, this instrument can perform analysis under ambient light, and the possible disturbance of the chemiluminescent emission is avoided. The instability of R6G and the kinetic behaviour of its dimeric and monomeric species in the chemiluminescent reaction are discussed.

2. Experimental details

2.1. Chemicals

Bis(2,4,5-trichlorophenyl-6-carboisopentyloxyphenyl)oxalate (TCPPO) and tetrabutylsalicylate (TBAS) (catalyst) were synthesized and purified following the procedures of Zhao [5]. R6G was obtained from Merck. Hydrogen peroxide (90%) (H_2O_2) was concentrated from commercial 30% H_2O_2 by vacuum distillation. Stock solutions of TCPPO (0.066 M), R6G (0.266 mM) and the catalyst were prepared in dibutylphthalate, while H_2O_2 (1.02 M) was dissolved in dimethylphthalate.

2.2. Absorption spectrum measurement

A photodiode array (PDA) UV–visible spectrophotometer HP8452A (Hewlett Packard) was employed to obtain the absorption spectra. The chemiluminescent reaction was monitored spectroscopically in situ. For the study of the effect of light irradiation on R6G

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degradation, a 150 W xenon lamp was used for irradiation in the wavelength range 470–600 nm (bandpass filter) at right angles to the optical pathway of measurement. All experiments were carried out at room temperature, and dibutylphthalate was used as the reference blank.

All data files were stored on disks and data manipulations were carried out on an IBM/486 microcomputer connected to the instrument.

3. Results and discussion

R6G exhibits strong absorption in the visible region. In dibutylphthalate, its absorption maximum is at approximately 530 nm (Fig. 1). With increasing dye concentration, a new absorption peak appears at shorter wavelengths. Rhodamine dyes tend to dimerize at higher concentrations [6]. The dimer spectrum is composed of two bands with absorption maxima at higher and lower energies than that of the monomer, as expected from exciton theory [7].

Fig. 2(a) shows the degradation of R6G in the peroxyoxalate chemiluminescent reaction. Since the absorption bands of TCPPO and TBAS lie in the UV region, the absorption spectrum vs. time profile provides information on the change in R6G in the reaction. At the initial stage of the reaction, due to the high concentration of R6G, strong aggregation is observed. As the reaction proceeds, the maximum at 508 nm (mainly contributed by dimers) decreases with an obvious red shift (Fig. 2).

R6G is very unstable in the peroxyoxalate chemiluminescent system. Several aspects merit further discussion. At the initial stage of the reaction (0–100 min), although the 508 nm peak decreases and shifts towards

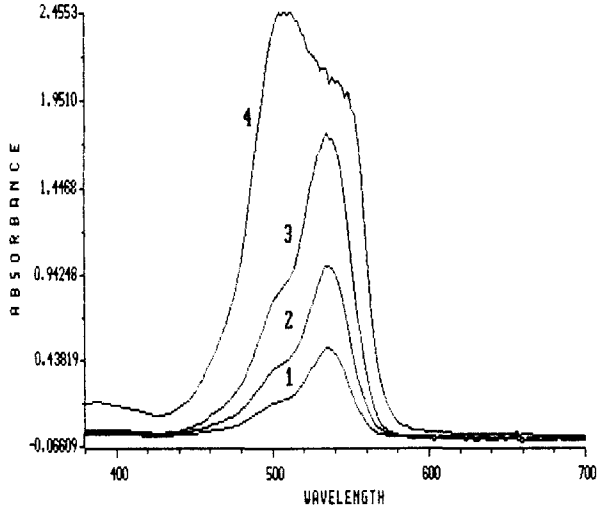

Fig. 1. Absorption spectra of R6G in dibutylphthalate. Dye concentration: 1, 6.7×10^{-6} M; 2, 1.3×10^{-5} M; 3, 2.7×10^{-5} M; 4, 8.0×10^{-5} M.

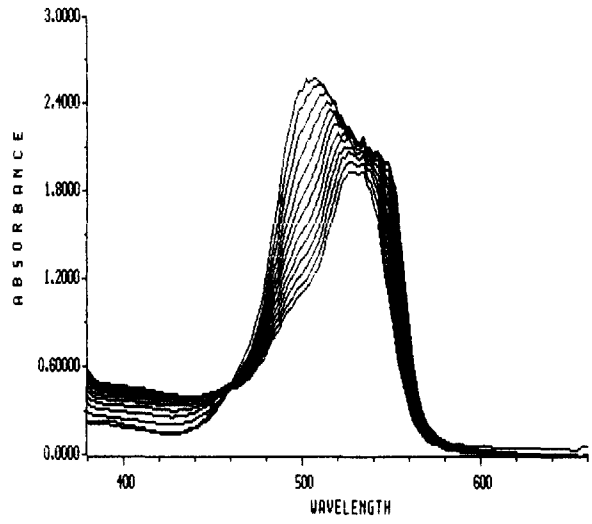

Fig. 2. Absorption spectrum vs. time profile showing the degradation of R6G. Every fifth curve is plotted. Conditions: 2.2×10^{-2} M TCPPO; 8.9×10^{-5} M R6G; 6.7×10^{-5} M TBAS; 0.2 M H_2O_2; the measurement lasted 3 h with a cycle of 3 min.

the red, the peak at about 530 nm remains almost unchanged. A careful observation shows that an isosbestic point exists at 464 nm at the initial stage of the reaction (Fig. 3(a)) which implies that, with the degradation of R6G, a new compound is formed with an absorption band at shorter wavelengths (overlapped by the absorption bands of the oxalate ester and the reaction products). Only dimeric species are degraded at this stage, otherwise the isosbestic point would not exist or would be shifted. This is due to the difference between the absorption spectra of monomeric and dimeric R6G molecules [6]. As expected, at the final stage of the reaction, when the monomeric maximum (approximately 530 nm) starts to decrease, the isosbestic point begins to shift to the blue (448 nm) (Fig. 3(b)).

It can be assumed that when there are only monomeric R6G molecules present in the solution, i.e. the dye at low concentration, the isosbestic point will be located at shorter wavelengths. This assumption was confirmed by the following experiment.

Fig. 4 exhibits the degradation of R6G at relatively low concentration (3.0×10^{-5} M). At such a low concentration, the dye monomer is the dominant species present in solution and the isosbestic point is shifted to 398 nm. It can be concluded that there is a preferential degradation of the dimeric species of R6G in the peroxyoxalate chemiluminescent system. This conclusion is consistent with the result obtained by Narang et al. [8], who studied the photoinstability of R6G on illumination.

A detailed analysis of Fig. 4(a) indicates that the absorbance at 530 nm ($A_{530\ nm}$) decreases via a two-exponential model (Fig. 4(b)), with a relatively fast component and a much slower component. This is similar to the light intensity/time course of peroxyoxalate

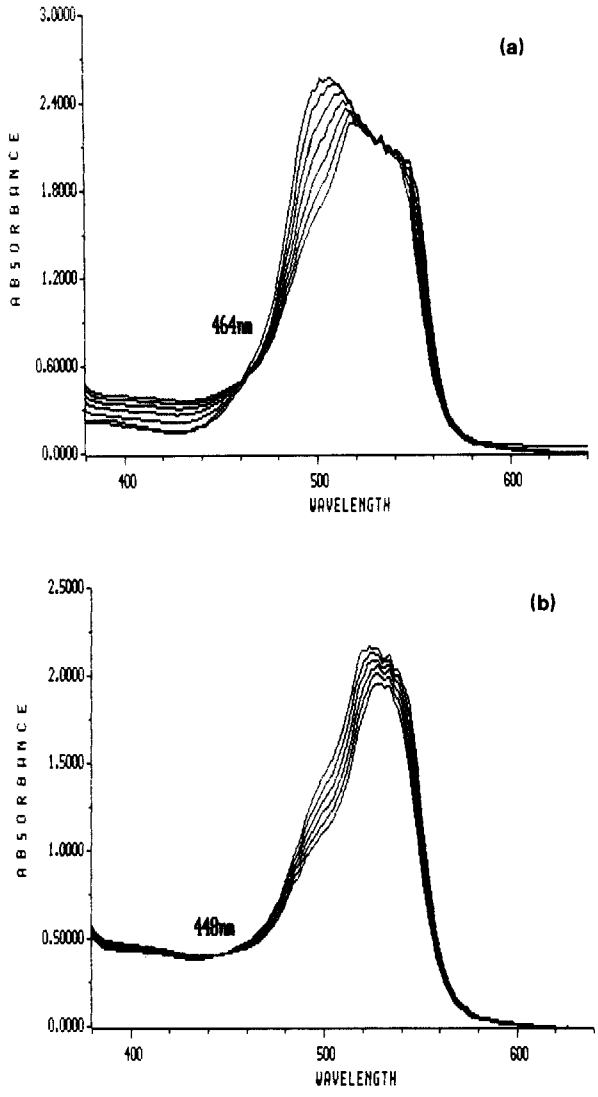

Fig. 3. (a) R6G degradation process at the initial stage. The isosbestic point is at 464 nm. (b) R6G degradation process at the final stage of the reaction. The isosbestic point is at 448 nm. Conditions: the same as shown in Fig. 2.

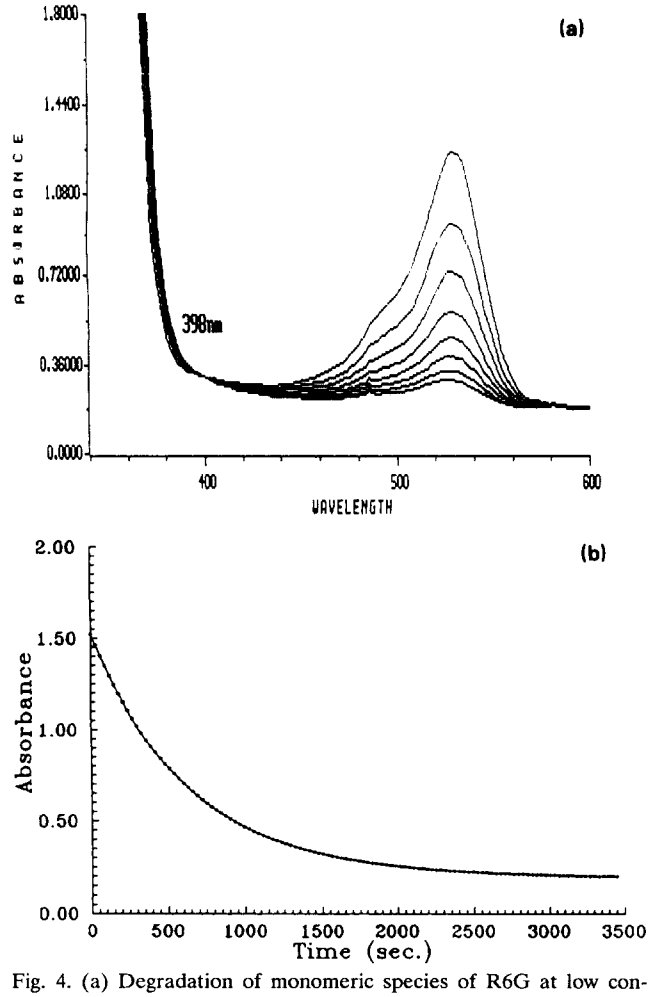

Fig. 4. (a) Degradation of monomeric species of R6G at low concentration. Every 15th curve is plotted. (b) Absorbance at 530 nm vs. time curve. Conditions: 0.015 M TCPPO; 0.001 M TBAS; 3.0×10^{-5} M R6G; 0.15 M H_2O_2. The test lasted 1 h with a cycle of 30 s.

chemiluminescence [9]. Such similarity indicates that further examination of the cause of the degradation of R6G in the reaction might offer valuable information on the mechanism of peroxyoxalate chemiluminescence.

Dye instability in peroxyoxalate chemiluminescence is usually thought to be caused by H_2O_2 oxidation, which is an active oxidant. However, our work has provided a contrary view. When only R6G and H_2O_2 were placed together, no R6G degradation was observed. In order to examine the influence of light on the stability of R6G, light radiation (470–600 nm) provided by a 150 W xenon lamp in conjunction with a bandpass filter was introduced. No change in the R6G absorption spectrum was observed during the measurement period (30 min).

It appears that the degradation of R6G is not caused by H_2O_2 oxidation; the role of H_2O_2 is insignificant judging from the rapid disappearance of R6G observed in our work. The isosbestic points (see above) indicate that, with the decrease in R6G (dimer or monomer), a new compound is formed. As the oxidative degradation of R6G by H_2O_2 and photodecomposition have been excluded, the degradation of R6G in the peroxyoxalate chemiluminescent reaction may be associated with the interaction between the fluorescer and the reaction intermediate(s). Further investigation is required to exploit the mechanism of degradation of R6G to aid in the understanding of the interaction of the fluorescer, and hence the pathway of energy transfer and the forms of the intermediate(s).

4. Conclusions

The dynamic degradation process of R6G in the peroxyoxalate chemiluminescent system was monitored. At high dye concentrations, two forms of R6G exist, monomeric and dimeric species, and the preferential

degradation of dimers is observed. The contributions of H_2O_2 and light irradiation to the degradation of the dye are insignificant; therefore dye degradation may be related to the interaction between the fluorescer and the reaction intermediates. Further study is under way.

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