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# A further study on the degradation mechanism of rhodamine 6G in the peroxyoxalate chemiluminescent reaction

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## Abstract

In previous work, we have demonstrated that the degradation of rhodamine 6G (R6G) in the peroxyoxalate chemiluminescent reaction may be related to the formation of an intermediate and that the oxidation effect of $H_2O_2$ is insignificant. In this paper, the effect of 9,10-diphenylanthracene (DPA) on the degradation of R6G has been examined. The experimental results show that, as the concentration of DPA is increased, the degradation rate of R6G decreases. This can be interpreted in terms of the competitive interaction of DPA and R6G molecules with the intermediate. It was also found that $N_2$ bubbling of the reaction mixture leads to a decrease in the degradation rate of R6G. On the basis of these experimental results, a mechanism for R6G degradation in the peroxyoxalate chemiluminescent system, involving a reaction intermediate and dissolved oxygen, is suggested.

*Keywords:* Degradation; Rhodamine 6G; Peroxyoxalate chemiluminescent reaction

## 1. Introduction

Much work has been reported on the mechanism of peroxyoxalate chemiluminescence [1–4]; however, some questions remain. One of these is the degradation mechanism of the fluorescer, such as rubrene and rhodamine [5].

In previous work [5], we have demonstrated that the degradation of rhodamine 6G (R6G) in a chemiluminescent system consisting of bis(2,4,5-trichlorophenyl-6-carboisopentyloxyphenyl)oxalate (TCPPO), $H_2O_2$ and tetrabutylammonium salicylate (TBAS) is not due to direct oxidation by $H_2O_2$ (at least such oxidative degradation is negligible), and the possible involvement of an intermediate has been suggested. We have explored the dye degradation mechanism in more detail in an attempt to elucidate the chemiluminescent reaction mechanism.

In this paper, the effect of the concentration of 9,10-diphenylanthracene (DPA) on the R6G degradation rate and the influence of dissolved oxygen were investigated. According to the chemically initiated electron exchange luminescence (CIEEL) mechanism [6,7], the reaction steps responsible for dye degradation were proposed.

## 2. Experimental details

### 2.1. *Chemicals*

TCPPO and TBAS (the catalyst) were synthesized and purified following the procedures of Zhao [8]. R6G and DPA were Merck products. Hydrogen peroxide ($H_2O_2$) (90%) was concentrated from commercial 30% $H_2O_2$ by vacuum distillation. Stock solutions of TCPPO (0.074 M), R6G (0.266 mM), DPA (0.012 M) 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. All experiments were carried out at room temperature, and dibutylphthalate was used as the reference blank. For $N_2$ bubbling tests, the desired amounts of TCPPO, R6G,

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TBAS and solvent were pipetted into a 1 cm quartz cell and bubbled with nitrogen for 10 min; hydrogen peroxide was added; the cell was shaken and inserted into the cell holder, starting spectrum sampling at the same time. The total volume of the reaction solution was adjusted by the solvent to 2 ml.

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

### 3.1. *Effect of DPA concentration*

In the peroxyoxalate chemiluminescent reaction, the molecules of the fluorescer are excited by interaction with the reaction intermediate. It can be imagined that, when more than one fluorescer is present in the reaction mixture, there will be competition for reaction with the intermediate between the different dyes. If the degradation of R6G is due to reaction with the intermediate [5], the presence of another dye will lead to a decrease in the degradation rate of R6G by reducing its chance of direct reaction with the intermediate. Since it is a relatively stable fluorescer, DPA was employed as the second dye.

The change in R6G concentration was monitored at 530 nm. The R6G concentration vs. reaction time curves are shown in Fig. 1. It can be seen that the addition of DPA causes a decrease in the degradation rate of R6G, which offers indirect evidence supporting the hypothesis that interaction between R6G molecules and the intermediate induces dye fading.

The introduction of DPA also leads to an increase in R6G fluorescence intensity. The different emission wavelength ranges of DPA (blue) and R6G (yellow) enabled the fluorescence intensities of the two dyes to be detected simultaneously with the help of a multichannel detector charge coupled device (CCD) in combination with a branched fibreoptic bundle equipped with two bandpass filters. It was found that the emission intensity of R6G increased with the addition of DPA. This is mainly due to possible energy transfer from the excited DPA molecules to the ground R6G molecules; hence more excited R6G molecules are produced compared with that in the absence of DPA. Since the degradation rate of R6G is reduced by the introduction of DPA (Fig. 1), it appears that the reaction process responsible for dye degradation is not related to the excited state of R6G, which is consistent with previous results [5].

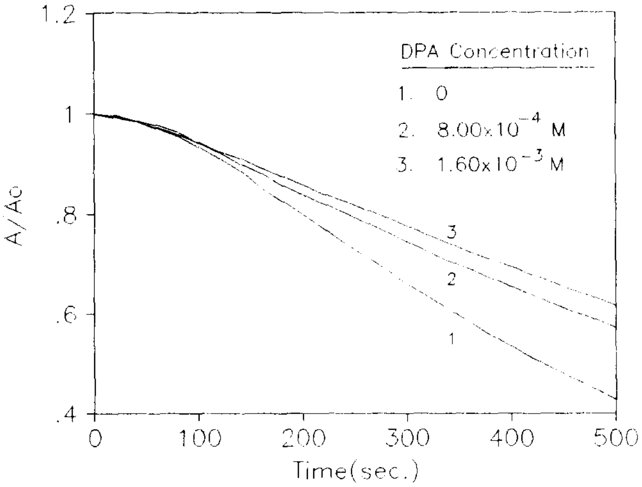

Fig. 1. Effect of DPA on the degradation rate of R6G: $1.48\times10^{-2}$ M TCPPO; 0.204 M $H_2O_2$; $5.12\times10^{-6}$ M R6G; $3.00\times10^{-3}$ M TBAS; the sampling cycle was 10 s.

### 3.2. *Effect of $O_2$ concentration*

Dissolved oxygen is a potential candidate causing R6G degradation. To determine the possible effect of dissolved oxygen on dye degradation, two sets of experiments, with and without $N_2$ bubbling, were carried out. The absorbance at 530 nm vs. time profiles were extracted and the initial degradation rates of R6G were obtained by statistical treatment. The results are shown in Table 1. It can be seen from Table 1 that the degradation rate of R6G is decreased after $N_2$ bubbling. It appears that dissolved oxygen does participate in the reactions leading to the degradation of R6G.

### 3.3. *Theoretical discussions*

Of the different mechanisms proposed for the peroxyoxalate chemiluminescent reaction, the CIEEL mechanism is the most popular, which was first proposed by Schuster [6,7]. Although it does not provide information on the number and identity of the reaction intermediates, the CIEEL mechanism does offer a satisfactory explanation for the relationship between the efficiency of peroxyoxalate chemiluminescence and the oxidation potential of the fluorescer, and yields an exact description of the energy transfer process occurring between the reaction intermediate and the fluorescer molecules. According to the CIEEL mechanism, there is an electron exchange process between the intermediate (X) and the fluorescer (ACT)

$$X + ACT \rightleftharpoons (XACT) \rightleftharpoons \underset{\mathbf{I}}{(X^{\cdot -}ACT^{\cdot +})} \xrightarrow[-CO_2]{}$$

$$\underset{\mathbf{II}}{(X'^{\cdot -}ACT^{\cdot +})} \longrightarrow X' + ACT^* \qquad (1)$$

Eq. (1) reveals that the excitation of the fluorescer involves two electron transfer processes. First, the intermediate receives an electron from the fluorescer,

Table 1
Influence of $N_2$ bubbling on the initial rates of R6G degradation

| | $N_2$ bubbling | No $N_2$ bubbling |
|---|---|---|
| $V_0$ ($s^{-1}$) | $2.19\times10^{-4}$, $1.31\times10^{-4}$, $3.11\times10^{-4}$ | $4.56\times10^{-4}$, $5.17\times10^{-4}$, $5.34\times10^{-4}$ |
| $\bar{V}_0$ ($s^{-1}$) | $2.20\times10^{-4}$ | $5.06\times10^{-4}$ |

Concentrations: $7.40\times10^{-3}$ M TCPPO, $2.00\times10^{-3}$ M TBAS, 0.102 M $H_2O_2$, $5.12\times10^{-6}$ M R6G.

forming the radical pair **I**. The fragmentation of the radical anion results in the formation of the radical pair **II** with the release of $CO_2$; the subsequent transfer of an electron back to the radical cation generates the excited fluorescer. It is suggested that electron exchange takes place within the solvent cage, which has been confirmed by results on the influence of the solvent viscosity on the reaction efficiency [1]. However, the diffusion of radicals **I** and/or **II** (Eq. (1)) may result in the separation of the radical pairs and the release of radicals from the solvent cage into the bulk of the solution. Therefore the following radical reactions are possibly present in the solution, and may be responsible for the consumption of the fluorescer

$$X^{\cdot -} + O_2 \longrightarrow X + O_2^{\cdot -} \qquad (2)$$

$$X'^{\cdot -} + O_2 \longrightarrow X' + O_2^{\cdot -} \qquad (3)$$

$$ACT^{\cdot +} + O_2^{\cdot -} \longrightarrow ACT\text{–}O_2 \qquad (4)$$

This scheme can explain the dependence of R6G on the dissolved oxygen and the presence of another dye (a rival of R6G for intermediate X). Radical reactions involving singlet oxygen, $^1O_2$, are excluded. This is because no consumption of R6G was observed, even under strong light irradiation [5], where singlet oxygen may be produced due to the sensitization of R6G. It is not known why red dyes are relatively unstable during the chemiluminescent reaction [9], e.g. R6G, rubrene and rhodamine B. Further studies are required.

## 4. Conclusions

The effects of DPA and $N_2$ bubbling on the degradation of R6G during the peroxyoxalate chemiluminescent reaction were examined. The presence of another dye leads to a decrease in the degradation rate of R6G. This can be explained by competition between the two dyes for interaction with the reaction intermediate, confirming the hypothesis that dye degradation is related to the formation of a reaction intermediate. The $N_2$ bubbling experiments proved that the degradation of R6G is associated with dissolved oxygen. According to the CIEEL mechanism, possible radical reactions responsible for dye degradation were suggested.

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