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Chemiluminescent Reaction between Polyphenols and Ozone in Acetic Acid

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The chemiluminescence of polyphenols with ozone in acetic acid was investigated in the presence and in the absence of rhodamine B. The emission intensity in the presence of rhodamine B (I_M) was about 100—500 times as large as that in the absence of the dye (I_P). From the measurement of the emission intensity *vs.* the reaction time, it was found that the time required to attain the peak intensity of I_M is almost equal to that required to attain the peak of I_P at equal concentration of polyphenol. A similarity was found in the spectral distributions of I_M and the fluorescence emission of rhodamine B determined under comparable conditions. Rhodamine B was scarcely decomposed for the production of the enhanced emission; this lent support to the conclusion that the enhancement effect of rhodamine B is due to an energy-transfer from an excited species produced by the oxidation of polyphenols to the dye. Determining the changes in the absorption spectra during the luminescent reaction, we also found that the emission results not from the decomposition of polyphenols but from the decomposition of an intermediate compound. On the basis of these results, a reaction scheme was proposed. If the increment of the total light emitted by the enhancement effect, (Δ), is defined as:

Δ=(Total light emitted in the polyphenol+rhodamine B system)−(Total light emitted in polyphenol alone)−(Total light emitted in rhodamine B alone),

the scheme gave the following equation:

$$\Delta = A[\mathrm{R}]_0 \ln(1+[\mathrm{P}]_0/A[\mathrm{R}]_0) \quad (1)$$

where $[\mathrm{R}]_0$ and $[\mathrm{P}]_0$ are the initial concentrations of rhodamine B and polyphenols respectively. A is the parameter, depending upon the experimental conditions. The values of Δ calculated from Eq. (1) were in fairly good agreement with the measured values.

In connection with the study of the ozonolysis of aromatic compounds, we are interested in the chemiluminescent reaction between ozone and such polyphenols as hydroquinone, resorcinol, catechol, pyrogallol, phloroglucinol, and gallic acid. However, little is yet known as to the mechanism for the chemiluminescent reaction because of the low photon yield.

In 1960, Bersis[1] showed that the emission intensity of the polyphenol chemiluminescence was remarkably enhanced in the presence of rhodamine B. Recently, Kamiya and Iwaki[2] have found that the emission from the reaction of eosin with hydrogen peroxide in an alkaline solution is enhanced by adding uranin. On the basis of kinetic studies, a mechanism involving an energy-transfer from an excited intermediate species*1 produced by the oxidation of eosin to uranin was postulated. Similar effects have been observed by several investigators: Kautsky and Zocher[3] found the effect of rhodamine dyes in the chemiluminescence of siloxen ($Si_6H_3O_6$) with potassium permanganate, and Vasil'ev[4] observed a similar effect of anthracene derivatives in the chemiluminescent autoxidation of hydrocarbon. In all of these reports, an energy-transfer mechanism was postulated to explain the enhanced emission. The present experimental results lend support to the postulation.

The spectral distribution of the enhanced emission agreed with that of the fluorescence emission

1) D. S. Bersis, *Z. Phys. Chem. (Neue Folge)*, **26**, 259 (1960).

2) I. Kamiya and R. Iwaki, This Bulletin, **39**, 269 (1966).

*1 Recently, the present authors have detected the intermediate species by means of a careful measurement of the spectra of the eosin chemiluminescence.

3) H. Zocher and H. Kautsky, *Z. Phys.*, **9**, 267 (1922).

4) R. F. Vasil'ev, *Nature*, **169**, 668 (1962).

of the added fluorescer, which was scarcely decomposed in the production of the enhanced emission.

As has been pointed out by Vasil'ev[5] and by Kasha[6], it is very suggestive that the behavior of excited species in an extremely weak chemiluminescent reaction can be investigated by means of the enhancing technique. In practice, several investigators[7] have carried out studies of weak chemiluminescent reactions by adding suitable fluorescers.

In the present paper, we will describe several experimental results supporting the theory that the enhancement effect of rhodamine B upon the emission of polyphenol chemiluminescence is caused by an energy-transfer excitation. The mechanism for the reaction, based on the kinetic results on the emission intensity, the emission spectra, and the changes in the absorption spectra during the luminescent reactions, will also be discussed.

Experimental

Original concentrated solutions of polyphenols (2.4×10^{-3} mol/l) and rhodamine B (1.6×10^{-3} mol/l) in acetic acid were diluted by adding acetic acid before they were used. Rhodamine B was recrystallized from a 60—70% aqueous ethanol solution. Analytical-grade polyphenols were used without further purification.

Reaction was initiated by introducing ozonized air produced in a Siemens ozonizer. Air was supplied by using a small rotary compressor, to which a manometer and a flowmeter were attached to control the pressure and the flow rate. The air was freed from carbon dioxide by granulated potassium hydroxide and dried by silica gel. Ozonized air was freed from the oxides of nitrogen (if any) by passing it through an aqueous solution of sodium hydroxide. The emitted light was detected with a photomultiplier tube (Toshiba MS9SY) coupled with a linear amplifier, and the output current was lead to a pen-recorder, so that the curves of the emission intensity *vs.* the reaction time could be recorded. Care was taken to keep constant the temperature (30°C) in the ozonizer and in the reaction vessel. The spectra of both the chemiluminescence and fluorescence were measured at 30°C, as has been described in a preceding paper.[8]

The absorption spectra of the reaction systems were measured with a Shimadzu SV-50-type recording spectrophotometer after the dissolved ozone had been removed by passing the systems through nitrogen gas. The concentrations of reactants and products were determined photometrically with a Shimadzu QR-50-type spectrophotometer.

Results

Curves of Emission Instensity *vs.* Reaction Time. The curves of the emission intensity *vs.* the reaction time measured in the rhodamine B system (I_R - t curve), in the gallic acid system (I_P - t

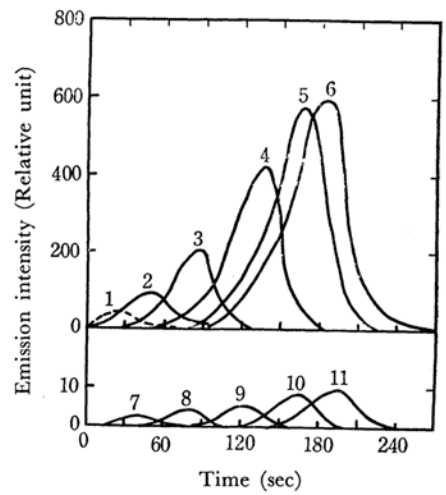

Fig. 1. Curves of emission intensity *vs.* the reaction time in gallic acid systems.
1: I_R (0-1-9), 2: I_M (1-1-8), 3: I_M (3-1-6), 4: I_M (5-1-4), 5: I_M (7-1-2), 6: I_M (9-1-0), 7: I_P (1-0-9), 8: I_P (3-0-7), 9: I_P (5-0-5), 10: I_P (7-0-3), 11: I_P (9-0-1)

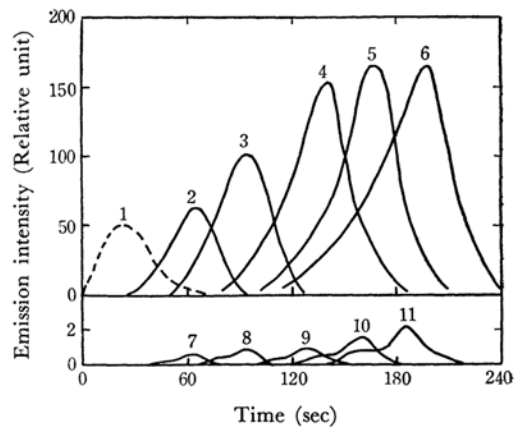

Fig. 2. Curves of emission intensity *vs.* the reaction time in resorcinol systems.
1: I_R (0-1-9), 2: I_M (1-1-8), 3: I_M (3-1-6), 4: I_M (5-1-4), 5: I_M (7-1-2), 6: I_M (9-1-0), 7: I_P (1-0-9), 8: I_P (3-0-7), 9: I_P (5-0-5), 10: I_P (7-0-3), 11: I_P (9-0-1)

5) R. F. Vasil'ev, *Optika i Spectroskopiya (Optics and Spectroscopy)*, **18**, 236, 416 (1965); *Photochem. Photobiol.*, **6**, 35 (1967).

6) A. U. Kahan and M. Kasha, *J. Am. Chem. Soc.*, **88**, 1674 (1966).

7) H. Linschitz, "Light and Life," John Hopkins Press, Baltimore (1961), p. 173; G. Lundeen and R. Livingstone, *Photochem. Photobiol.*, **4**, 1085 (1965); J. Stauff, *ibid.*, **4**, 1199 (1965); L. J. Bollyky, H. H. Whitman, R. A. Clarke and M. M. Rauhut, *J. Org. Chem.*, **32**, 1663 (1967).

8) I. Kamiya and R. Iwaki, This Bulletin, **39**, 264 (1966).

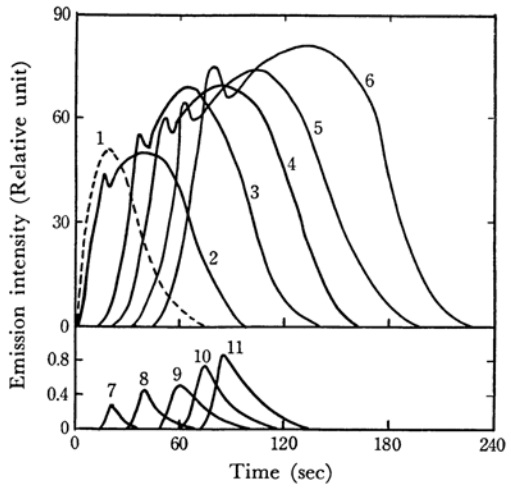

Fig. 3. Curves of emission intensity *vs.* the reaction time in hydroquinone systems.
1: I_R (0-1-9), 2: I_M (1-1-8), 3: I_M (3-1-6), 4: I_M (5-1-4), 5: I_M (7-1-2), 6: I_M (9-1-0), 7: I_P (1-0-9), 8: I_P (3-0-7), 9: I_P (5-0-5), 10: I_P (7-0-3), 11: I_P (9-0-1)

curve), and in the gallic acid system in the presence of rhodamine B (I_M - t curve) are given in Fig. 1, where (x-y-z) refers to the system composed of x m*l* of the polyphenol solution, y m*l* of the rhodamine B solution, and z m*l* of acetic acid. These results indicate that: (1) In both emissions, with and without enhancing, the emission rises to a maximum value (I_{max}) after a period of induction, and then slowly decreases.

(2) In the two systems of equal initial concentrations of polyphenol, the I_{max} of the I_M - t curve is almost 100—500 times as large as that of the I_P-t curve, but the time required to attain the I_{max} (τ) of I_M is nearly equal to that needed to attain that of I_P.

(3) Both values of I_{max} and τ increase with an increase in the concentration of polyphenol.

The curves of the emission intensity measured in resorcinol systems are given in Fig. 2. Similar curves were obtained in catechol systems. Figure 2 shows that the emission characteristics are apparently similar to those in gallic acid, but are not so intense.

Figure 3 shows the emission characteristics measured in hydroquinone systems, demonstrating that I_M - t curves have two emission peaks while I_P- t curves have only one peak. It may be noted that the time required to attain the first peak of the I_P - t curve is almost equal to the time required to attain the I_{max} of I_P - t curve in each pair with equal concentrations of polyphenol.

Similar curves were obtained in the pyrogallol and phloroglucinol systems, but the emission is more intense than that in the hydroquinone system.

The effect of the rhodamine B concentration upon the emission intensity was measured in both the gallic acid system and the hydroquinone system. The results, shown in Figs. 4 and 5 respectively, indicate that the values of I_{max} increase with an increase in the concentration of rhodamine B, but the values of τ hardly vary if the polyphenol concentration is ketp constant.

Figure 6 shows the effect of the rhodamine B concentration upon the I_R - t curve, demonstrating that the induction period is neither so long nor so varied after the change in the initial concentration of rhodamine B as that found in polyphenol chemiluminescence.

Chemiluminescence Spectra. The chemiluminescence spectra were determined in gallic acid and pholoroglucinol system containing rhodamine B, and were compared with the fluorescence spectrum of rhodamine B determined under comparable conditions. As may be seen in Fig. 7 (the gallic acid system) and Fig. 8 (the phloroglucinol

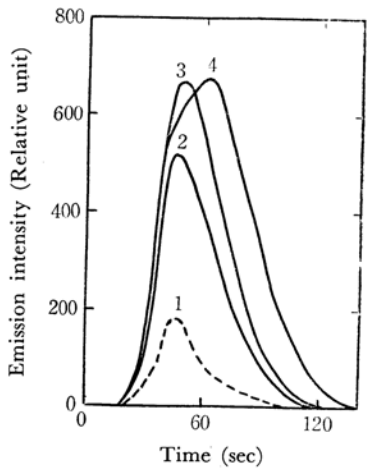

Fig. 4. The effect of rhodamine B concentration upon the I_M - t curves for gallic acid systems.
1: $I_P \times 200$(7-0-3), 2: I_M (7-1-2), 3: I_M (7-2-1), 4: I_M (7-3-0)

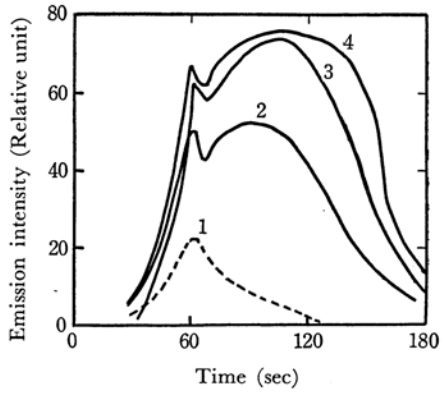

Fig. 5. The effect of rhodamine B upon the I_M - t curves for hydroquinone systems.
1: $I_P \times 200$(7-0-3), 2: I_M (7-1/2-5/2), 3: I_M (7-1-2), 4: I_M (7-2-1)

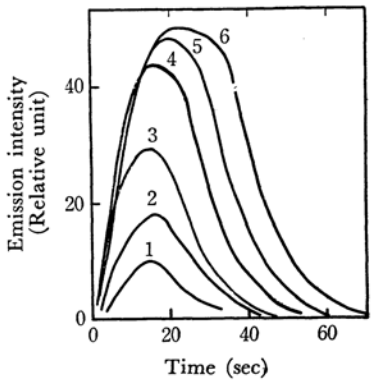

Fig. 6. The effect of rhodamine B concentration upon $I_R - t$ curves.
Curve 1: 8.0×10^{-6} mol/l
Curve 2: 1.6×10^{-5} mol/l
Curve 3: 3.2×10^{-5} mol/l
Curve 4: 6.4×10^{-5} mol/l
Curve 5: 9.6×10^{-5} mol/l
Curve 6: 1.6×10^{-4} mol/l

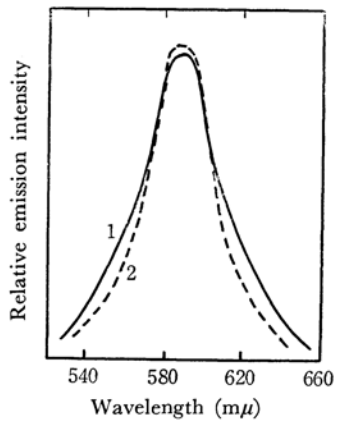

Fig. 7. Chemiluminescence spectrum in gallic acid - rhodamine B system and fluorescence spectrum of rhodamine B.
Curve 1: chemiluminescence
Curve 2: fluorescence

system), similar chemiluminescence and fluorescence spectral distributions were obtained, indicating that the excited singlet of rhodamine B is the emitting species.

Changes in Absorption Spectra of Polyphenol in the Region between 250 mμ and 450 mμ during the Luminescence Reaction. The absorption spectrum of hydroquinone in acetic acid was changed during the oxidation with ozone, as is shown in Fig. 9. The peak at 291 mμ decreased, and simultaneously a new band at about 250 mμ appeared to reach a maximum, which was then decreased by oxidation. The changes can be attributed to both the decomposition of hydroquinone and the formation of an intermediate compound. Figure 10 shows the plots of $\log D_{291}$

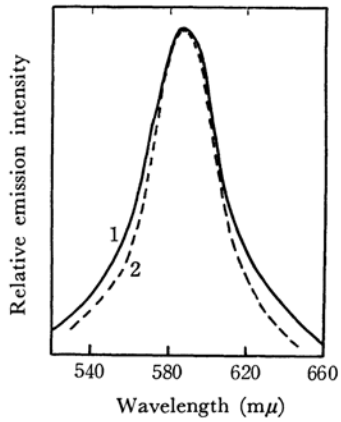

Fig. 8. Chemiluminescence spectrum in phloroglucinol - rhodamine B system and fluorescence spectrum of rhodamine B.
Curve 1: chemiluminescence
Curve 2: fluorescence

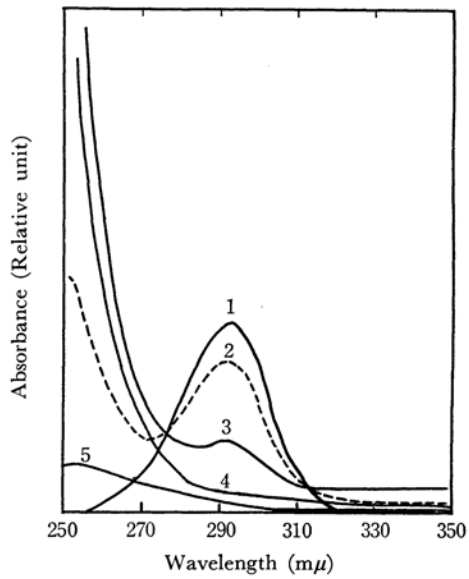

Fig. 9. Change in absorption spectra of hydroquinone system during the luminescent reaction (1→2→3→4→5).

(absorbance at 291 mμ) against the reaction time. The plots on the straight line indicate that the decomposition of hydroquinone from the initial stage of the reaction is first order with respect to the polyphenol concentration. The plots of D_{250} *vs.* reaction time are shown in Fig. 11. It is demonstrated that the decomposition processes are not so simple because the time required to attain the maximum concentration of the intermediate compound increases with an increase in the initial concentration of hydroquinone.

Figure 12 shows the changes in the absorption spectrum of gallic acid during the oxidation with

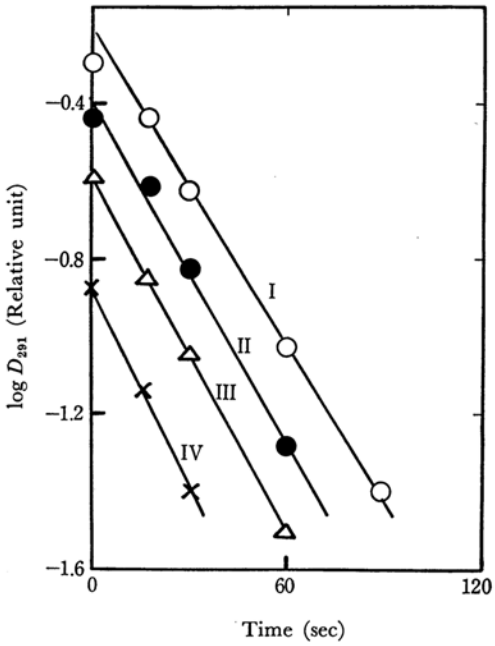

Fig. 10. Plots of $\log D_{291}$ against the reaction time in the several systems of various initial concentrations of hydroquinone ($[P]_0$).
Curve I: $[P]_0=2.2\times10^{-3}$ mol/l
Curve II: 1.7×10^{-3} mol/l
Curve III: 1.2×10^{-3} mol/l
Curve IV: 7.2×10^{-4} mol/l

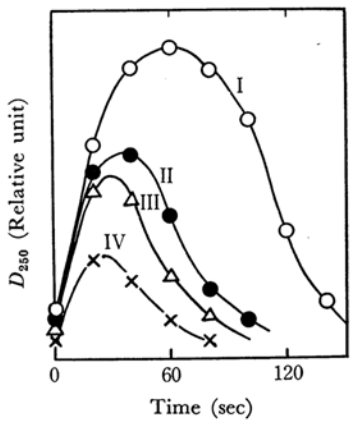

Fig. 11. Plots of D_{250} against the reaction time in the several systems of various initial concentrations of hydroquinone ($[P]_0$).
Curve I: $[P]_0=2.2\times10^{-3}$ mol/l
Curve II: 1.7×10^{-3} mol/l
Curve III: 1.2×10^{-3} mol/l
Curve IV: 7.2×10^{-4} mol/l

ozone. The results show that the peak at 272 mμ decreases without the appearance of a new absorption peak. However, the changes in the absorbance at 340 mμ (D_{340}), shown in Fig. 13, strongly suggest the formation of an intermediate compound. The plots of $\log D_{272}$ *vs.* the reaction time, given in Fig. 14, demonstrate that the decomposition of gallic acid at the initial stage is also first order with respect to the polyphenol concentration.

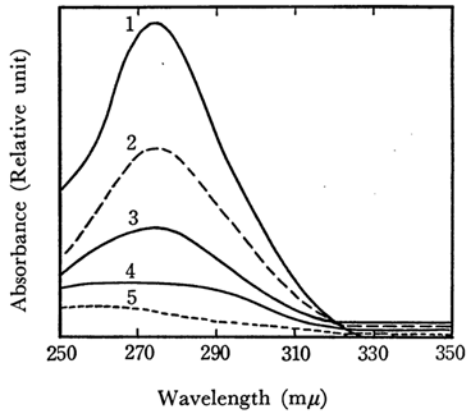

Fig. 12. Changes in absorption spectra of a gallic acid system during the luminescent reaction (1→2→3→4→5).

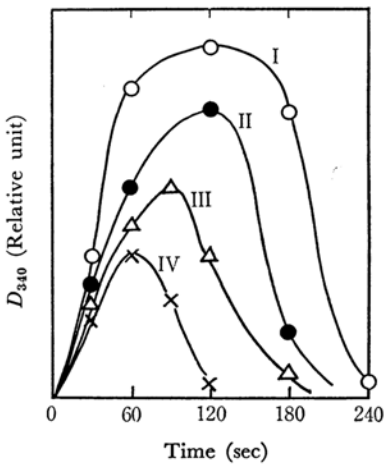

Fig. 13. Plots of D_{340} against the reaction time in the several systems of various initial concentrations of gallic acid ($[P]_0$).
Curve I: $[P]_0=2.2\times10^{-3}$ mol/l
Curve II: 1.7×10^{-3} mol/l
Curve III: 1.2×10^{-3} mol/l
Curve IV: 7.2×10^{-4} mol/l

In resorcinol systems, the changes in the absorption spectrum were not so simple as those in hydroquinone and gallic acid.

Decomposition Rate of Rhodamine B. Figure 15 shows the changes in the concentration of rhodamine B during the luminescent reaction in hydroquinone-rhodamine B systems. It is important and interesting to see that rhodamine B hardly decomposes at all until the hydroquinone decreases upon its oxidation with ozone to a low concentration; this means that the enhanced

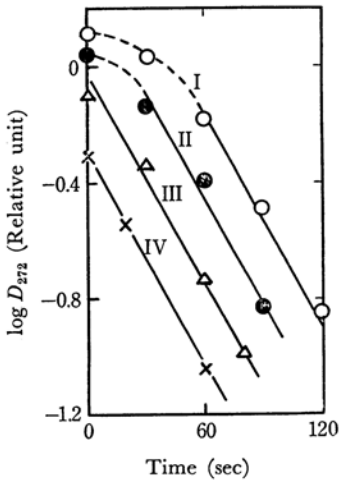

Fig. 14. Plots of $\log D_{272}$ against the reaction time in the several systems of various initial concentrations of gallic acid ($[P]_0$).
Curve I: $[P]_0=2.2\times10^{-3}$ mol/l
Curve II: 1.7×10^{-3} mol/l
Curve III: 1.2×10^{-3} mol/l
Curve IV: 7.2×10^{-4} mol/l

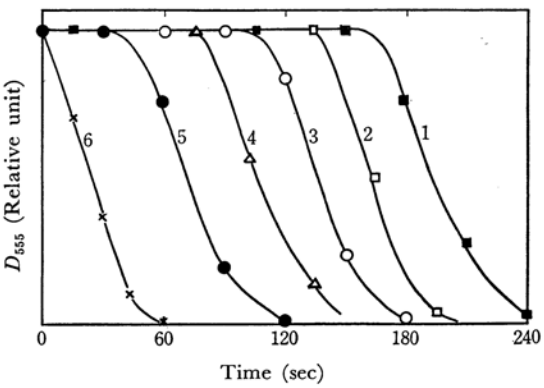

Fig. 15. The concentration of rhodamine B as a function of the reaction time in the several systems of various initial concentrations of hydroquinone.
1: (9-1-0), 2: (7-1-2), 3: (5-1-4),
4: (3-1-6), 5: (1-1-8), 6: (0-1-9)

emission does not result from the decomposition of the dye. The decomposition-curves of rhodamine B measured in other polyphenol-systems are shown in Fig. 16; they demonstrate that all of the polyphenols retard the decomposition of rhodamine B as hydroquinone does.

Discussion

The experimental results apparently indicate that the enhancement effect of rhodamine B upon the chemiluminescence of polyphenols is caused by an energy-transfer from an excited species produced by the reaction of polyphenols to the dye.

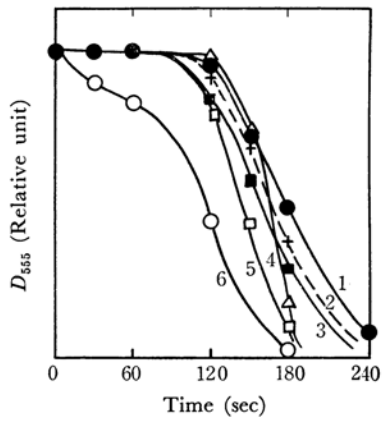

Fig. 16. The concentration of rhodamine B as a function of the reaction time in the several systems of various polyphenols. Initial concentrations of polyphenol and rhodamine B are 2.2×10^{-3} mol/l and 1.6×10^{-4} mol/l, respectively.
1: Catechol, 2: Hydroquinone,
3: Resorcinol, 4: Phloroglucinol,
5: Pyrogallol, 6: Gallic acid

The I_M - t curves with the changes in the concentrations of gallic acid and of the intermediate compound are compared in Fig. 17. It is found that the I_M - t curve does not agree with the decomposition curve of hydroquinone, but does agree with that of the intermediate compound except for the initial stage. This fact indicates that the polyphenol chemiluminescence arises not from the

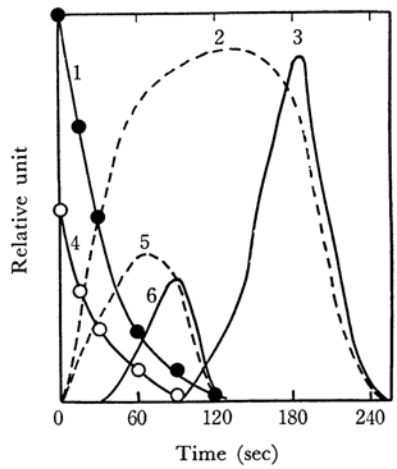

Fig. 17. Comparison between I_M - t curve and concentration curve of gallic acid or intermediate compound in gallic acid systems.
1: $[P]$ - t curve (9-1-0)
2: D_{340} - t curve (9-0-1)
3: I_M - t curve (9-1-0)
4: $[P]$ - t curve (3-1-6)
5: D_{340} - t curve (3-0-7)
6: I_M - t curve (3-1-6)

decomposition of the gallic acid but from the decomposition of the intermediate. The discrepancy for the initial stage in the two curves can be explained by the argument that the decomposition of the intermediate is retarded by polyphenol, as is that of rhodamine B. This argument is supported by the experimental findings to be described below.

A solution of polyphenol was pre-treated for a short duration with ozone in order to lower the concentration of polyphenol; then nitrogen gas was bubbled into it to remove the dissolved ozone. After rhodamine B had been added to the pre-treated solution, ozone was again passed into the solution to initiate the luminescent reaction. The curves of the emission intensity *vs.* the reaction time measured in such pre-treated solutions of gallic acid and hydroquinone are shown in Figs. 18 and 19 respectively. These figures show that the induction periods for the luminescent reactions were shortened by the pre-treatment. Moreover, when small amounts of the polyphenols were added again to the pre-treated solution, the emission was observed after a long induction period, as is shown by dotted curves in Figs. 18 and 19.

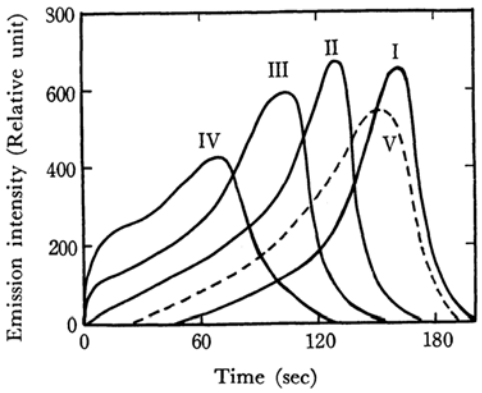

Fig. 18. I_M - t curves measured in gallic acid systems, pre-treated with ozone.
I: non-treated, II: treated for 30 sec, III: 60 sec, IV: 120 sec, V: A small amount of gallic acid was added after pre-treated for 120 sec.

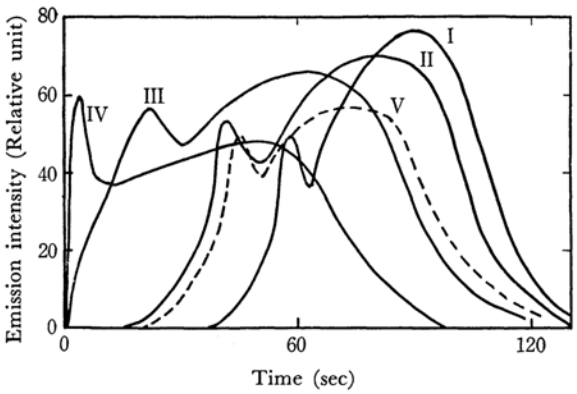

Fig. 19. I_M - t curves measured in hydroquinone systems, pre-treated with ozone.
I: non-treated, II: treated for 30 sec, III: 45 sec, IV: 60 sec, V: A small amount of hydroquinone was added after pre-treated for 60 sec.

As is shown in Fig. 3, the first peak of the I_M - t curves and the peak of the corresponding I_R - t curves are found at the same reaction time. In view of the finding that the polyphenols do retard the decomposition of rhodamine B, it seems liekly that the first peak of the I_M - t curve is to be attributed to the enhanced emission due to an energy-transfer (say, I_{PR}-emission), and the second peak, to the luminescent decomposition of rhodamine B (say, I'_R-emission).

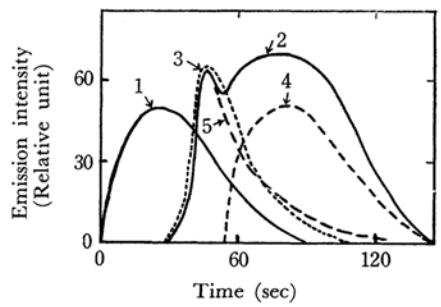

Fig. 20. Curves of I_R, I_M and I_P and shematic curves of I'_R- and I_{PR}-emission in hydroquinone systems.
1: I_R (0-1-9), 2: I_M (5-1-4), 3: I_P (5-0-5)×100, 4: I'_R-emission, 5: I_{PR}-emission

If the curve of the I'_R-emission is assumed to be described by the parallel displacement of the I_R - t curve measured for rhodamine B alone, so as to fit the decay part with the I_M - t curve measured in the polyphenol - rhodamine B system, the schematic curve of I_{PR} - emission can be obtained graphically by subtracting the curve of the I'_R-emission from the I_M - t curve. Figure 20 shows the curves of the I'_R-emission and the I_{PR}-emission described in this way, together with the I_P - t curve measured in polyphenol alone. We can see in Fig. 20 that the curve of I_{PR}-emission is very similar to the I_P - t curve.

Two peaks did not appear in the I_M - t curves for gallic acid. This is probably due to the fact that the I'_R-emission falls upon the I_{PR}-emission as a result of the weak retardation for rhodamine B decomposition.

Reaction Scheme

On the basis of the results, the following mechanism seems plausible for the luminescent reaction:

At the initial stage, polyphenol (P) is oxidized with ozone to produce an intermediate compound

(M):

$$P \xrightarrow{O_3} M \qquad [I];\ \text{reaction rate: } k_1.$$

The polyphenol concentration [P] at the reaction time t is given by:

$$[P] = [P]_0 \exp(-k_1 t) \tag{1}$$

where $[P]_0$ is the initial concentration of polyphenol. Taking account of the fact that M does not decompose until [P] becomes small value of $[P]' = [P]_0 \exp(-k_1 t')$, we have:

$$[M] = [P]_0\{1-\exp(-k_1 t')\} \tag{2}$$

when $t \leqq t'$. Assuming that t' is nearly equal to τ (the time required to attain I_{max}), the values of [P]′ can be calculated from $[P]' = [P]_0 \exp(-k_1 \tau)$ by using the values of τ measured in hydroquinone systems for various $[P]_0$ and k_1 values; these values are tabluated in Table 1. The values of [P]′ are almost constant, which indicates that our presumption is plasusible.

Table 1. The values of [P]′ calculated from the equation, $[P]' = [P]_0 \exp(-k_1 \tau)$ in hydroquinone systems

$[P]_0$ (mol/l)	k_1 (sec^{-1})	τ (sec)	[P]′ (mol/l)
2.4×10^{-4}	0.032	17	1.4×10^{-4}
7.2×10^{-4}	0.032	34	2.4×10^{-4}
1.2×10^{-3}	0.032	48	2.6×10^{-4}
1.7×10^{-3}	0.032	60	2.5×10^{-4}
2.2×10^{-3}	0.032	72	2.2×10^{-4}
2.4×10^{-4}	0.045	15	1.2×10^{-4}
7.2×10^{-4}	0.045	27	2.1×10^{-4}
1.2×10^{-3}	0.045	37	2.3×10^{-4}
1.7×10^{-3}	0.045	45	2.2×10^{-4}
2.2×10^{-3}	0.045	52	2.1×10^{-4}

For the sake of simplicity, we may write the production of an excited species (S*) in the following first-order reaction with respect to the concentration of the intermediate compound:

$$M \xrightarrow{O_3} S^* \qquad [II];\ k_2.$$

Thus, when $t>t'$, [M] is given by:

$$[M] = [\{(k_1-k_2)[P]_0 + k_2[P]'\}\exp(-k_2 T) - k_1[P]'\exp(-k_1 T)]/(k_1-k_2) \tag{3}$$

where $T=t-t'$.

S* is deactivated by fluorescence processes or by non-radiative processes:

$$S^* \longrightarrow S + h\nu \qquad [III];\ k_3.$$
$$S^* \longrightarrow S \qquad [IV];\ k_4.$$
$$S^* + M \rightarrow S + M \qquad [V];\ k_5.$$
$$S^* + P \rightarrow S + P \qquad [VI];\ k_6.$$

In the systems involving rhodamine B (R), the processes of energy-transfer from S* to R take place:

$$S^* + R \rightarrow S + R^* \qquad [VII];\ k_7.$$

R* is deactivated by the fluorescence process:

$$R^* \longrightarrow R + h\nu' \qquad [VIII];\ k_8.$$

Although other non-radiative processes of deactivation also take place, our discussion is limited to the process VIII because of the high efficiency of the fluorescence emission of R. The intensity of emission resulting from the energy-transfer (I_{PR}) is given by:

$$I_{PR} = k_8[R^*] = k_7[S^*][R] \tag{4}$$

where [R] is the rhodamine B concentration.

By the steady-state approximation, $d[S^*]/dt=0$, and assuming that $k_5=k_6=k_q$ and $k_3+k_4 \ll k_7[R]+k_q([M]+[P])$, [S*] is given by:

$$[S^*] = k_2[M]/\{k_7[R] + k_q([M] + [P])\} \tag{5}$$

From Eqs. (3), (4), and (5), I_{PR} is given by:

$$I_{PR} = \frac{k_2k_7[R][\{(k_1-k_2)[P]_0+k_2[P]'\}\exp(-k_2T)-k_1[P]'\exp(-k_1T)]}{(k_1-k_2)k_7[R]+k_q[\{(k_1-k_2)[P]_0+k_2[P]'\}\exp(-k_2T)-k_2(P)'\exp(-k_1T)]} \tag{6}$$

The values of Δ (the increment in the total light emitted by the enhancement effect) is defined as:

$$\Delta = \int_0^\infty (I_M - I_P - I_R)dT \tag{7}$$

Using the relations: $I_M = I_{PR} + I'_R$ and $I_M \gg I_P$, and assuming that $\int I_R dT = \int I'_R dT$ and $[R]=[R]_0$ (the initial concentration of rhodamine B), Eq. (7) becomes:

$$\Delta = \int_0^\infty I_{PR}dT = (k_7/k_q)[R]_0 \ln\{1+[P]_0/(k_7/k_q)[R]_0\} \tag{8}$$

Equation (8) is reduced to the following convenient form:

$$\Delta = A[R]_0 \ln(1+[P]_0/A[R]_0) \tag{9}$$

where $A=k_7/k_q$. Table 2 illustrates the values of Δ measured by using the graphical integration of I_M-t curves and I_R-t curves and the values calculated from Eq. (9) by using a suitable parameter A. The calculated values are in fairly good agreement with the measured values in every polyphenol systems.

A similar chemiluminescence emission and the enhancement effect of rhodamine B were observed

TABLE 2. OBSERVED AND CALCULATED Δ-VALUES IN THE SEVERAL SYSTEMS OF DIFFERENT POLYPHENOLS
$\Delta_{calc.}=A[R]_0\ln(1+[P]_0/A[R]_0)$

Phenol	$[P]_0$ (mol/l)	$[R]_0$ (mol/l)	A	$\Delta_{calc.}\times10^6$	$\Delta_{obs.}\times10^6$
Resorcinol	2.4×10^{-4}	8.0×10^{-6}	5.0	78	81
	2.4×10^{-4}	1.6×10^{-5}	5.0	121	147
	2.4×10^{-4}	3.2×10^{-5}	5.0	147	182
	2.4×10^{-4}	6.4×10^{-5}	5.0	179	166
Catechol	2.4×10^{-4}	8.0×10^{-6}	19	145	145
	2.4×10^{-4}	1.6×10^{-5}	19	175	188
	2.4×10^{-4}	3.2×10^{-5}	19	200	191
	2.4×10^{-4}	6.4×10^{-5}	19	208	225
Hydroquinone	2.4×10^{-4}	8.0×10^{-6}	5.55	83	83
	2.4×10^{-4}	1.6×10^{-5}	5.55	115	117
	2.4×10^{-4}	3.2×10^{-5}	5.55	150	159
	2.4×10^{-4}	6.4×10^{-5}	5.55	189	163
	2.4×10^{-4}	9.6×10^{-5}	5.55	195	179
Phloroglucinol	2.4×10^{-4}	8.0×10^{-6}	40	177	179
	2.4×10^{-4}	1.6×10^{-5}	40	202	207
	2.4×10^{-4}	3.2×10^{-5}	40	207	207
	2.4×10^{-4}	6.4×10^{-5}	40	230	230
	2.4×10^{-4}	1.1×10^{-4}	40	242	251
Gallic acid	1.2×10^{-3}	1.6×10^{-6}	15	69	94
	1.2×10^{-3}	4.0×10^{-6}	15	191	184
	1.2×10^{-3}	8.0×10^{-6}	15	340	288
	1.2×10^{-3}	1.6×10^{-5}	15	432	430
	1.2×10^{-3}	8.0×10^{-5}	15	684	828
	1.2×10^{-3}	1.6×10^{-4}	15	989	971

in the solutions of aminophenols and phenylenediamine in acetic acid, but neither emission nor enhancement effect was observed in the phenol, aniline, nitrophenol, and nitroaniline system. The enhancement effect upon the polyphenol chemiluminescence emission was also observed when anthracene was added in place of rhodamine B, but no enhancement effect was observed in the presence of methylene blue. Further investigation is necessary to elucidate these phenomena.