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Degradation of Azo Dyes by Sodium Hypochlorite 3. Estimation of the Rate Equation for the Degradation of Orange G and Benzopurpurine

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Degradation of azo dyes, Orange G and Benzopurpurine, by sodium hypochlorite in water was observed by UV spectroscopy. The observed values of the maximum absorbance in the spectra of the reaction mixture fitted well with the polynomials of the fifth degree in reaction time, t. The initial degradation rate of each dye was obtained easily as the differential coefficient of the functions at time 0. The degradation rate (R_d) of both dyes in the initial stage of the reaction was given by the second-order rate equation, $R_d=k[\mathrm{Dye}][\mathrm{NaOCl}]$, where k is a rate constant. Apparent activation energies and frequency factors of the degradation were estimated as 20.3 kJ mol^{-1} and 4.59×10^4 dm^3 mol^{-1} s^{-1}, respectively, for Orange G, and 9.56 kJ mol^{-1} and 5.78×10^3 dm^3 mol^{-1} s^{-1} for Benzopurpurine.

Sodium hypochlorite (NaOCl) is extensively used for bleaching colored impurities in many kinds of materials.[1)] In addition, the fastness of water-soluble azo dyes to chlorine is a very important requirement in the dyeing industry. However, the mechanism of the degradation of the substances by NaOCl has not been understood well because of the complexity of the reaction. In general, the spectroscopy is very convenient for checking the fading of dyes by NaOCl. Gregory and Stend estimated the half-life time for water-soluble azo dyes in the spectral change of the mixture of the dyes and NaOCl in water and discussed the relation between the stability of the dyes and their molecular structures.[2)] Their method is very convenient, but is not available for the estimation of exact kinetic values. We observed the spectral change of the mixture of several dyes and NaOCl in water and found that the fading curves of the dyes were represented by equations of the fifth degree in reaction time, t.[3)] In the present research, the kinetic investigation was carried out for the degradation of a mono azo dye, Orange G and a bisazo dye, Benzopurpurine by NaOCl. After the change of reactants with time is obtained by curves, the differential method is available to estimate the initial reaction rate. Although this is considered to be the most reliable method to know the reaction rates, it involves the measurements of tangents to the concentration–time curves, which sometimes makes it difficult to determine the exact reaction rates.[4)] However, the reaction rate in the initial stage can be easily obtained as the differential coefficients of the functions at time, 0, if the change of reactants is given by a function of the third degree in reaction time in some organic reactions.[5)] In the present study, the degradation of each of the two dyes by NaOCl was observed by the spectroscopy, and the curve fitting was carried out for the observed absorbance change with time in the spectra. The initial degradation rates of the dyes by NaOCl were estimated by the differentiation of the fitted equations, and the rate equations, frequency factors and apparent activation energies for the reactions were estimated.

Experimental

Materials. Orange G (OG: C.I. Acid Orange 10) of Wako Pure Chemical Industries, Ltd. and Benzopurpurine (BP: C.I. Direct Red 2) of Tokyo Chemical Industries Ltd. were dried in vacuo and were used without further purifications. Sodium hypochlorite (NaOCl) was a commercial reagent grade product of Wako Pure Chemical Industries, Ltd. ; the chlorine content was checked by the usual method before use.[6)] A buffer solution of pH 8 was prepared with water, borax (Kanto Chemical Industries, Ltd.) and hydrochloric acid (Yoneyama Reagent Ind. Co., Ltd.) in the usual manner.[7)]

Spectroscopy. A Shimadzu UV-2200 spectrophotometer was employed. Each dye and NaOCl were dissolved in the buffer solution of pH 8. The dye solution (4 ml) was mixed rapidly with the NaOCl solution (1 ml) and the measurement of the absorbance change with time was started at 12 s to 18 s after the mixing. The range of [OG] in the reaction mixture was 1.71×10^{-5}— 4.28×10^{-5} mol dm^{-3}, that of [NaOCl] 2.14×10^{-4}— 1.72×10^{-3} mol dm^{-3}, and that of [BP] 2.29×10^{-5}— 4.62×10^{-5} mol dm^{-3}.

Results and Discussion

Figures 1 and 2 give the spectral changes of the mixture of OG and NaOCl in water and that of BP and NaOCl. The OG mixture gives a maximum absorption at 478 nm and the BP mixture at 498 nm. The absorption peak of the OG mixture at 478 nm is considered to be due to the hydrazone tautomer of the dye.[2)] These absorption peaks diminish as the reaction of the dyes with NaOCl proceeds. Since the scanning for each spec-

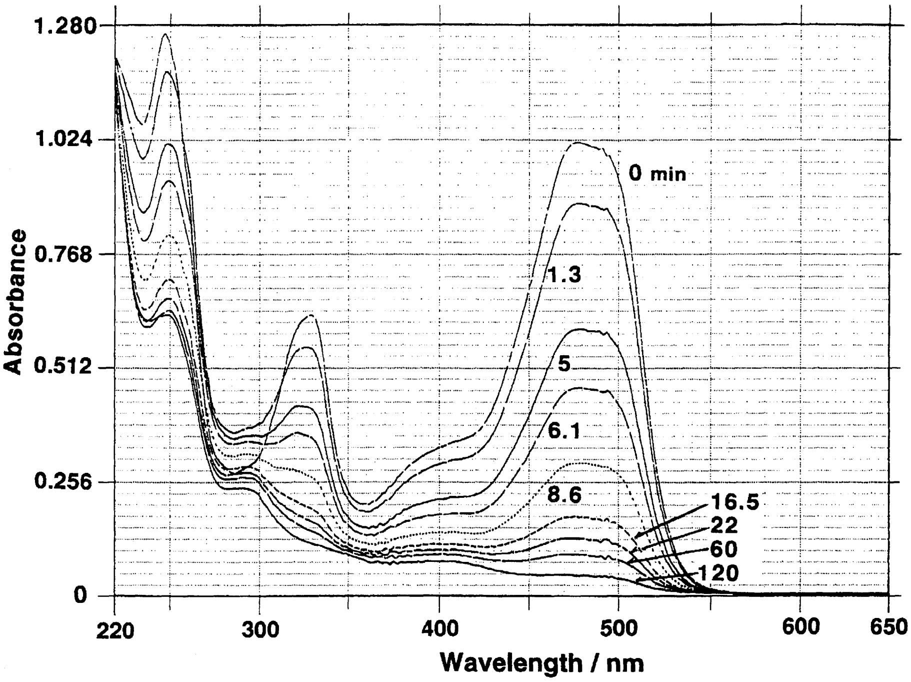

Fig. 1. Time change of the spectra of the mixture of OG and NaOCl in water. The numbers on each spectrum give the time in min when the absorbance at 478 nm was recorded; the spectrum at 0 min is before addition of NaOCl. $[OG]_0$: 4.29×10^{-5} mol dm^{-3}, $[NaOCl]_0/[OG]_0$: 6.86 and temp 20 °C.

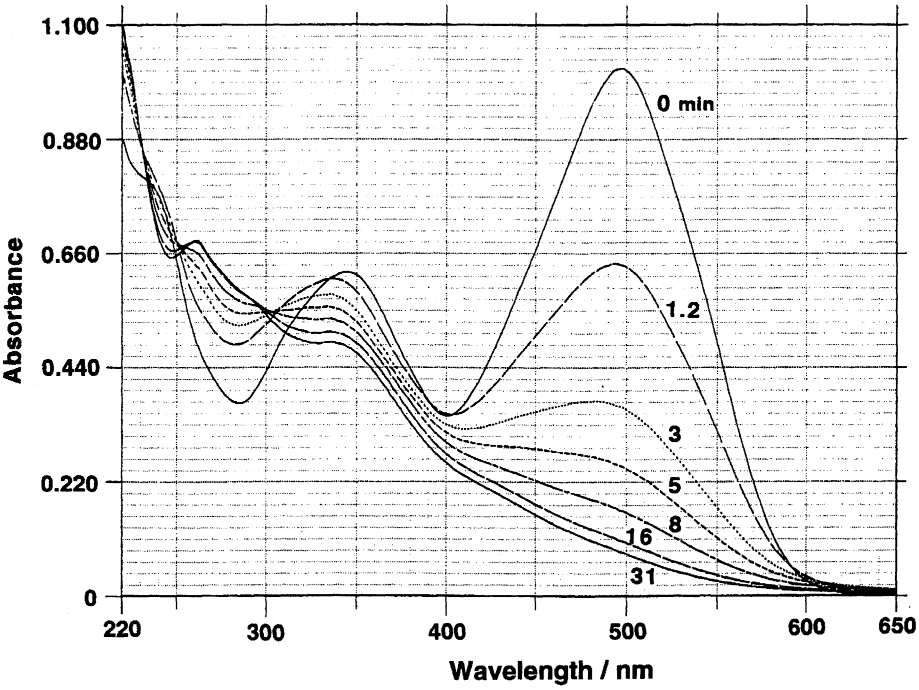

Fig. 2. Time change of the spectra of the mixture of BP and NaOCl in water. The numbers on each spectrum give the time in min when the absorbance at 498 nm was recorded; the spectrum at 0 min is before addition of NaOCl. $[BP]_0$: 4.24×10^{-5} mol dm^{-3}, $[NaOCl]_0/[BP]_0$: 4.00 and temp 20 °C.

trum of Figs. 1 and 2 took about 2 min, only the change of these maximum absorptions with time was observed to see the fading rate of each dye in the reaction mixture. These changes were obtained experimentally as the fading curves of the dyes. The fading curves of the degradation of OG by NaOCl in water were obtained as the initial concentration of OG ($[\mathrm{OG}]_0$) was changed and that of NaOCl ($[\mathrm{NaOCl}]_0$) was constant. A curve fitting for the observed data was carried out by a computer using a least squares method.[8] As a result, the observed absorbances at 478 nm of the reaction mixture fit well with the polynomials of the fifth degree in a variable, t. Thus, the equations which were fit to the data were in the form,

$$\text{Absorbance} = a_0 + a_1 t + a_2 t^2 + a_3 t^3 + a_4 t^4 + a_5 t^5, \qquad (1)$$

where a_0, a_1, a_2, a_3, a_4, and a_5 are regression coefficients and t is the time in min. In Fig. 3, the symbols (○, △ etc.) give the observed absorbances at 478 nm of the reaction mixture and the curves represent the fitted equations. Table 1 gives each of the coefficients of the polynomials in the fitted equations and the coefficient of determination, R^2 (a ratio of explained variation to total variation) in the curve fitting. The R^2 value, 1.0 in each analysis demonstrates the best fit between the observed data and the values calculated from each of the fitted equations. Thus, the initial degradation rate of the dye by NaOCl could be easily obtained as the negative of the differential coefficient of each of the fitted equations at time 0, i.e., $-a_1$. The double-logarithmic plot of $-a_1$ against the dye concentration gives a straight line with a slope of 1.00, as shown in Fig. 4. This implies that the fading rate of OG by NaOCl is proportional to the first power of [OG] in the initial stage of the reaction.

When the degradation rate of OG by NaOCl is of the first order with respect to [OG] under the condition of almost constant [NaOCl], a linear relationship should be

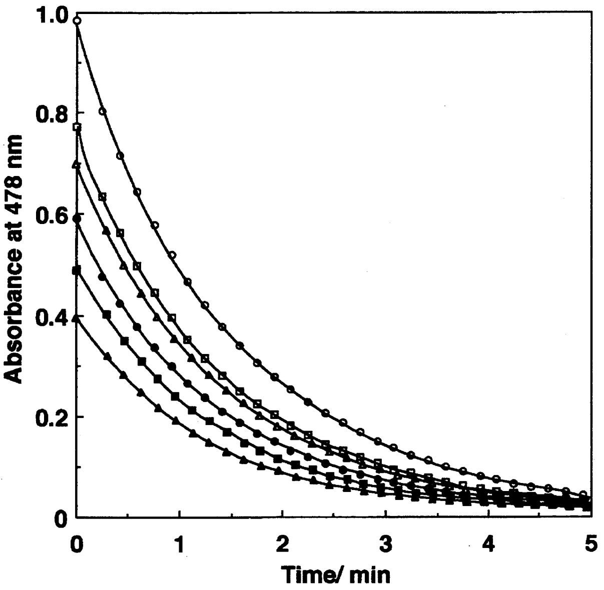

Fig. 3. Time change of the absorbance of the mixture of OG and NaOCl in water at 478 nm. The symbols are the observed data and the curves are the fitted equations. $[\mathrm{OG}]_0 \times 10^5$: 1.71 (○), 2.14 (□), 2.75 (△), 3.00 (●), 3.43 (■), 4.28 (▲) mol dm^{-3}, $[\mathrm{NaOCl}]_0$: 1.60×10^{-3} mol dm^{-3} and temp 20 °C.

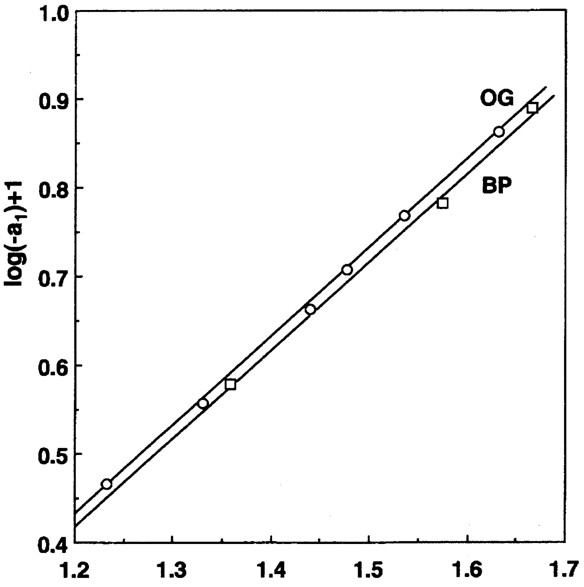

Fig. 4. Logarithmic plots between $-a_1$ and $[\mathrm{Dye}]_0$ with the data for OG given in Table 1 and those for BP given in Table 4.

Table 1. Coefficients of the Polynomials in the Fitted Equations Given in Fig. 3 and R^2 Factors in the Curve Fitting[a)]

$[\mathrm{OG}]_0 \times 10^5$ (mol dm^{-3})[b)]	$a_0 \times 10$	$a_1 \times 10$	$a_2 \times 10$	$a_3 \times 10^2$	$a_4 \times 10^3$	$a_5 \times 10^4$	R^2
4.28	9.78	−7.30	3.18	−9.11	14.5	−9.45	1.00
3.43	7.71	−5.86	2.39	−6.04	8.58	−5.08	1.00
3.00	6.97	−5.10	1.93	−4.58	6.25	−3.63	1.00
2.75	5.88	−4.60	1.98	−5.45	8.49	−5.46	1.00
2.14	4.92	−3.61	1.25	−2.43	2.51	−1.07	1.00
1.71	3.95	−2.93	0.977	−1.66	1.31	0.310	1.00

a) $[\mathrm{NaOCl}]_0$: 1.60×10^{-3} mol dm^{-3} and reaction temp: 20 °C. b) Subscript 0 means the initial concentration.

seen between the reaction time and $\ln([\mathrm{OG}]_0/[\mathrm{OG}]_t)$, in which $[\mathrm{OG}]_t$ is the concentration at time t, according to the first-order rate law.[9] We can use the absorbance data given in Fig. 3 for the plotting. The plot is seen to follow an almost straight line as given in Fig. 5. This result coincides with that of the above curve fitting method.

When the degradation of OG by NaOCl was carried out under the conditions of a great excess of $[\mathrm{OG}]_0$ to $[\mathrm{NaOCl}]_0$ and constant $[\mathrm{NaOCl}]_0$, the change of the absorbance of the dye in the course of the reaction was too small and too fast to be observed exactly by an ordinary spectrophotometer. Thus, the method of assuming a pseudo-first-order reaction was not applied for the determination of the order with respect to [NaOCl] in the present reaction.

The dependence of the degradation rate of OG by NaOCl on [NaOCl] was examined under the conditions of an excess of $[\mathrm{NaOCl}]_0$ to $[\mathrm{OG}]_0$ and constant $[\mathrm{OG}]_0$. The observed data and the fitted equations are represented by the symbols and the curves, respectively in Fig. 6. Each of the coefficients of the polynomials in the fitted equations and R^2 in the curve fitting is given in Table 2. The initial reaction rate is obtained as $-a_1$ by the differentiation of the equations. The double-logarithmic plot of $-a_1$ against [NaOCl] gives a straight line with a slope of 0.980, as shown in Fig. 7. Thus, the initial degradation rate of OG, R_{dOG} by NaOCl can be approximated by the following equation:

$$R_{\mathrm{dOG}} = k[\mathrm{OG}][\mathrm{NaOCl}]. \qquad (2)$$

A rate coefficient, k was estimated to be 7.54 $\mathrm{mol^{-1}\,dm^3\,s^{-1}}$ from Fig. 4. The present method is very useful for the estimation of the kinetics even in such a difficult case.

The temperature dependence of the degradation rate of OG by NaOCl was examined using constant $[\mathrm{OG}]_0$ and $[\mathrm{NaOCl}]_0$. Figure 8 gives the time change of the

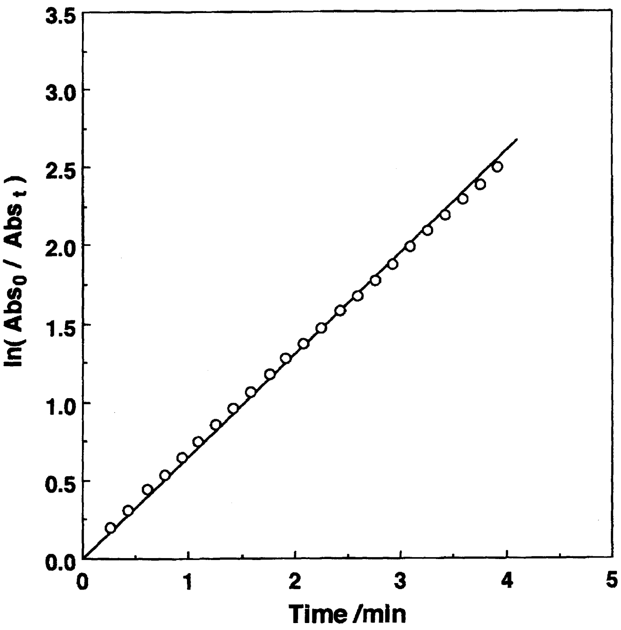

Fig. 5. Relation between $\ln(\mathrm{Abs}_0/\mathrm{Abs}_t)$ and time in the reaction of OG with NaOCl. $[\mathrm{OG}]_0$: 4.28×10^{-5} $\mathrm{mol\,dm^{-3}}$, $[\mathrm{NaOCl}]_0$: 1.30×10^{-3} $\mathrm{mol\,dm^{-3}}$ and temp 20 °C.

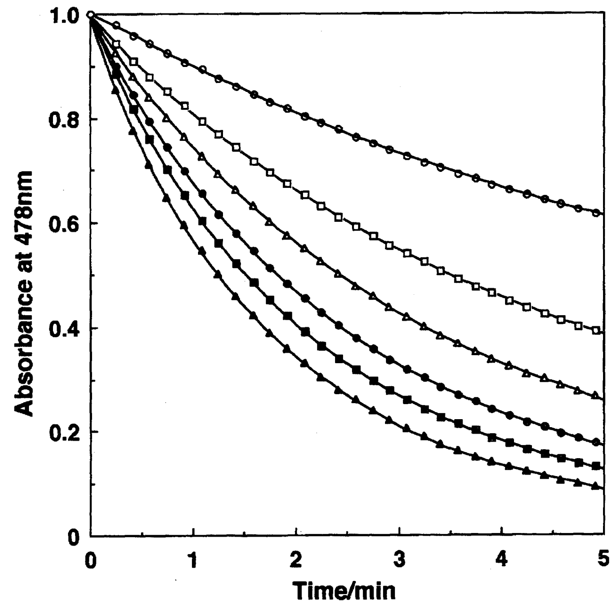

Fig. 6. Time change of the absorbance of the mixture of OG and NaOCl in water at 478 nm. The symbols are the observed data and the curves are the fitted equations. $[\mathrm{OG}]_0$: 4.28×10^{-5} $\mathrm{mol\,dm^{-3}}$, $[\mathrm{NaOCl}]_0/[\mathrm{OG}]_0$: 5.0 (○), 10 (□), 15 (△), 20 (●), 25 (■), 30 (▲), and temp 20 °C.

Table 2. Coefficients of the Polynomials in the Fitted Equations Given in Fig. 6 and R^2 Factors in the Curve Fitting[a]

$[\mathrm{NaOCl}]_0\times10^4$ ($\mathrm{mol\,dm^{-3}}$)	a_0	$a_1\times10$	$a_2\times10^2$	$a_3\times10^3$	$a_4\times10^3$	$a_5\times10^4$	R^2
2.14	1.00	−0.986	−0.692	6.48	−1.34	0.984	1.00
4.28	0.997	−2.23	4.04	−8.66	1.39	−0.949	1.00
6.43	0.998	−3.05	6.04	−11.6	1.75	−1.19	1.00
8.58	0.998	−4.03	9.88	−20.1	2.96	−1.99	1.00
11.1	0.998	−4.81	13.3	−2.65	3.46	−2.07	1.00
12.9	0.995	−6.05	22.7	−6.01	9.31	−5.99	1.00

a) $[\mathrm{OG}]_0$: 4.28×10^{-5} $\mathrm{mol\,dm^{-3}}$, reaction temp: 20 °C.

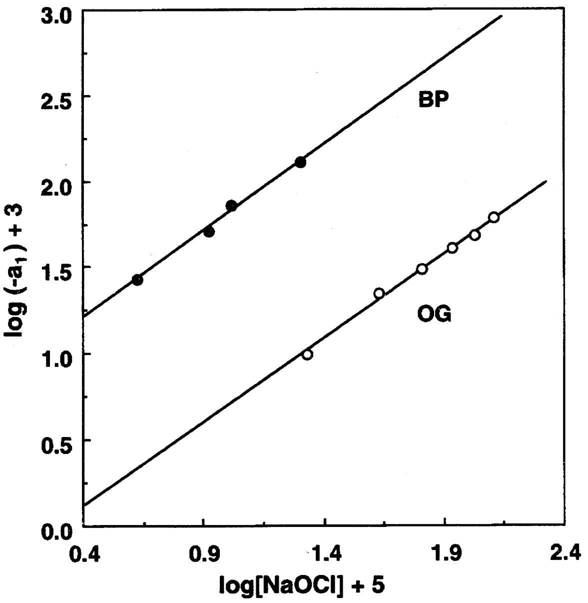

Fig. 7. Logarithmic plots between $-a_1$ and $[\mathrm{NaOCl}]_0$ with the data for OG in Table 2 and those of BP in Table 5.

absorbance at 478 nm of the reaction mixture at four temperatures. The fitted equations of the fifth degree in t are given by the curves in Fig. 8. The coefficients of the polynomials in the fitted equations and R^2 in the curve fitting are given in Table 3. The initial degradation rates of OG by NaOCl at the four temperatures were obtained by $-a_1$ as relative values. Figure 9 gives the Arrhenius plot. The apparent activation energy and frequency factor for the degradation of OG by NaOCl are estimated to be 20.3 kJ mol^{-1} (4.84 kcal mol^{-1}) and 4.59×10^4 dm^3 mol^{-1} s^{-1}, respectively.

The kinetic study on the degradation of BP by NaOCl in water was also carried out by the same manner as that of OG. The absorbance at 498 nm of the reaction mixture was observed when $[\mathrm{BP}]_0$ was changed and $[\mathrm{NaOCl}]_0$ was constant. The observed data also fit well with the equations of the fifth degree in t, as shown by Eq. 1. The coefficients of the polynomials in the fitted equations and R^2 in the curve fitting are given in Table 4. The initial degradation rates of BP by NaOCl are also given by $-a_1$. The double-logarithmic plot of $-a_1$ against [BP] gave a straight line with a slope of 0.999, as shown in Fig. 4.

The absorbance at 498 nm of the reaction mixture of

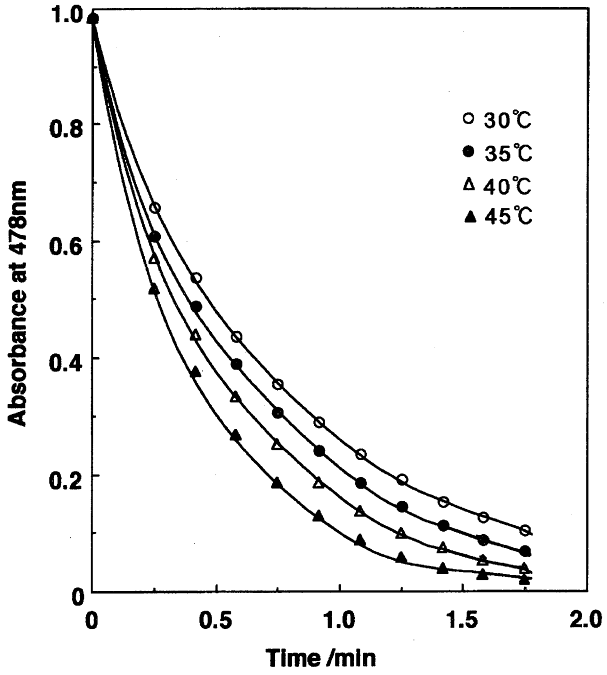

Fig. 8. Temperature dependence of the fading of the mixture of OG and NaOCl in water. $[\mathrm{OG}]_0$: 4.28×10^{-5} mol dm^{-3} and $[\mathrm{NaOCl}]_0$: 1.72×10^{-3} mol dm^{-3}. The symbols are the observed data and the curves are the fitted equations.

BP and NaOCl was observed when $[\mathrm{BP}]_0$ was constant and $[\mathrm{NaOCl}]_0$ was changed. The data were analyzed similarly to those of OG. The coefficients of the polynomials in the fitted equations and R^2 in the curve fitting are given in Table 5. The initial degradation rate of BP by NaOCl is also given by $-a_1$. The double-logarithmic plot of $-a_1$ against [NaOCl] gave a straight line with a slope of 1.01, which is shown in Fig. 7. These results suggest that the fading rate of BP by NaOCl is also given as follows:

$$R_{\mathrm{dBP}} = k'[\mathrm{BP}][\mathrm{NaOCl}]. \tag{3}$$

The rate constant, k' was estimated to be 125 mol^{-1} dm^3 s^{-1} from Fig. 4.

The temperature dependence of the fading rate of BP by NaOCl was also examined and the curve fittings for the observed absorbances were carried out similarly to OG. Table 6 gives the coefficients of the polynomials in the fitted equations and R^2 in the curve fitting. The

Table 3. Coefficients of the Polynomials in the Fitted Equations in Fig. 8 and R^2 Factors in the Curve Fitting[a)]

Temp/°C	a_0	a_1	$a_2\times10^2$	$a_3\times10^3$	$a_4\times10^4$	$a_5\times10^7$	R^2
30	0.984	−1.75	2.32	−2.13	1.04	−1.97	1.00
35	0.984	−2.13	3.35	−3.38	1.72	−3.34	1.00
40	0.984	−2.33	3.56	−3.42	1.69	−3.24	1.00
45	0.984	−2.66	4.16	−3.96	1.94	−3.72	1.00

a) $[\mathrm{OG}]_0$: 4.28×10^{-5} mol dm^{-3} and $[\mathrm{NaOCl}]_0$: 1.72×10^{-3} mol dm^{-3}.

Table 4. Coefficients of the Polynomials in the Fitted Equations to the Observed Absorbance Data and R^2 Factors in the Curve Fitting in the Reaction of BP with NaOCl when $[\mathrm{BP}]_0$ was Changed and $[\mathrm{NaOCl}]_0$ was Constant[a)]

$[\mathrm{BP}]_0\times10^5$ ($\mathrm{mol\,dm^{-3}}$)	$a_0\times10$	$a_1\times10$	$a_2\times10$	$a_3\times10^2$	$a_4\times10^3$	$a_5\times10^4$	R^2
4.62	10.9	−7.96	4.30	−12.9	19.4	−11.4	1.00
3.75	8.85	−6.15	2.94	−7.96	11.2	−6.32	1.00
2.29	5.39	−3.84	1.84	−4.95	6.88	−3.81	1.00

a) $[\mathrm{NaOCl}]_0$: 9.33×10^{-5} $\mathrm{mol\,dm^{-3}}$ and reaction temp: 20 °C.

Table 5. Coefficients of the Polynomials in the Fitted Equations to the Observed Absorbance Data and R^2 Factors in the Curve Fitting in the Reaction of BP with NaOCl when $[\mathrm{NaOCl}]_0$ was Changed and $[\mathrm{BP}]_0$ was Constant[a)]

$[\mathrm{NaOCl}]_0/[\mathrm{BP}]_0$	$a_0\times10$	$a_1\times10$	$a_2\times10$	$a_3\times10^2$	$a_4\times10^3$	$a_5\times10^4$	R^2
1.00	9.99	−2.76	0.864	−1.55	1.61	−0.835	1.00
2.00	9.98	−4.95	2.43	−7.88	14.0	−10.2	1.00
2.50	1.00	−6.90	3.56	−11.0	17.8	−11.5	1.00
5.00	9.99	−1.31	10.2	−41.6	83.3	−65.1	1.00

a) $[\mathrm{BP}]_0$: 4.24×10^{-5} $\mathrm{mol\,dm^{-3}}$ and reaction temp: 20 °C.

Table 6. Coefficients of the Polynomials in the Fitted Equations to the Observed Absorbance Data and R^2 Factors in the Curve Fitting in the Reaction of BP with NaOCl at Three Temperatures[a)]

Temp/°C	$a_0\times10$	$a_1\times10$	$a_2\times10$	$a_3\times10$	$a_4\times10^2$	$a_5\times10^3$	R^2
20	9.95	−7.23	4.64	−1.72	3.22	−2.35	1.00
30	9.94	−8.44	4.92	−1.57	2.52	−1.57	0.999
40	9.87	−9.67	6.07	−2.01	3.26	−2.04	0.999

a) $[\mathrm{BP}]_0$: 4.24×10^{-5} $\mathrm{mol\,dm^{-3}}$ and $[\mathrm{NaOCl}]_0$: 1.72×10^{-3} $\mathrm{mol\,dm^{-3}}$.

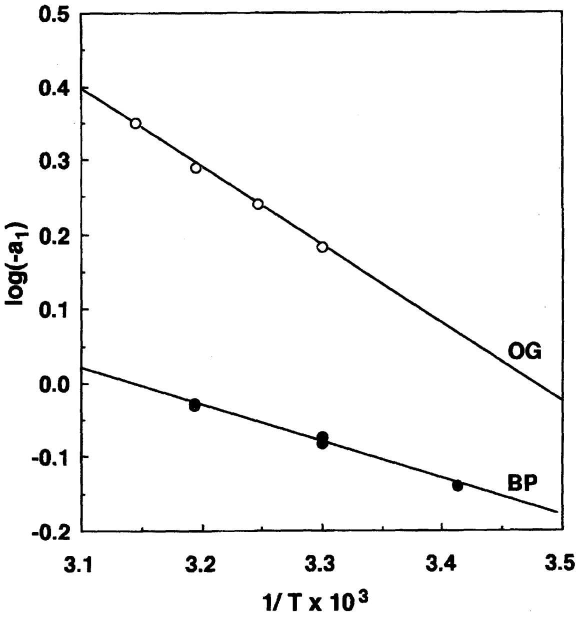

Fig. 9. Arrhenius plots using the $-a_1$ values of OG in Table 3 and those of BP in Table 6.

Arrhenius plot using the initial fading rates of BP, the $-a_1$ values, is given in Fig. 9. The apparent activation energy and the frequency factor for the degradation of BP by NaOCl are estimated to be 9.56 $\mathrm{kJ\,mol^{-1}}$ (2.29 $\mathrm{kcal\,mol^{-1}}$) and 5.78×10^3 $\mathrm{dm^3\,mol^{-1}\,s^{-1}}$, respectively. This activation energy is about a half of that of OG.

Conclusion

The fading curves of the reaction mixture of each of the dyes, OG and BP and NaOCl in the spectroscopic measurements were represented by the equations of the fifth degree polynomials with one variable, reaction time t. The initial degradation rates of the dyes by NaOCl were estimated easily by the differentiation method using these equations. This made it very easy to determine the rate equation and kinetic values such as rate constants, activation energies and frequency factors.

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