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PHOTOREDUCTION OF PHENAZINE BY CONTINUOUS LIGHT ILLUMINATION IN AQUEOUS SULFURIC ACID SOLUTION

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Phenazinium monocation was found to be converted into dihydrophenazine cation radical through $^1(\pi\pi^*)$ state by photoreduction with the quantum yield of 0.50 and 0.28 in aerated and deaerated aqueous sulfuric acid solutions, respectively, accompanying with the water decomposition followed by the formation of hydrogen peroxide. In the presence of oxygen, the photoproduct changes to 1-hydroxyphenazine by the dark reaction.

Phenazinium monocation (PH^+) is known to undergo photoreduction to produce dihydrophenazine cation radical ($PH_2^{\dot{+}}$) in strongly acidic methanol.$^{1)}$ Wake et al.$^{2)}$ also treated phenazinium monocation in the acidic aqueous solution, insisting on the direct photochemical formation of 1-hydroxyphenazine from the excited PH^+ and on the formation of 1:1 mixture of dihydrophenazine and 1-hydroxydihydrophenazine cation redicals.

We have investigated the photoreduction of PH^+ in the aqueous sulfuric acid solution. The results and the interpretation are, however, quite different from those of Wake et al.

It was confirmed that in the acidic aqueous solution only PH^+ undergoes photochemical reaction by the 365 nm illumination and that the other two forms (P and PH_2^{2+}) are stable. The absorption spectral change of PH^+ in the aqueous sulfuric acid solution is shown in Fig. 1. The peak of PH^+ at 383 nm decreases and that of the product at 443 nm increases with the illumination, accompanying an isosbestic point at 402 nm. The colorless solution turns to lime green with the reaction. Deaeration of the solutions does not affect the general feature of the reaction run and the photoproduct. The photoproduct was identified to $PH_2^{\dot{+}}$ from the comparison of the absorption

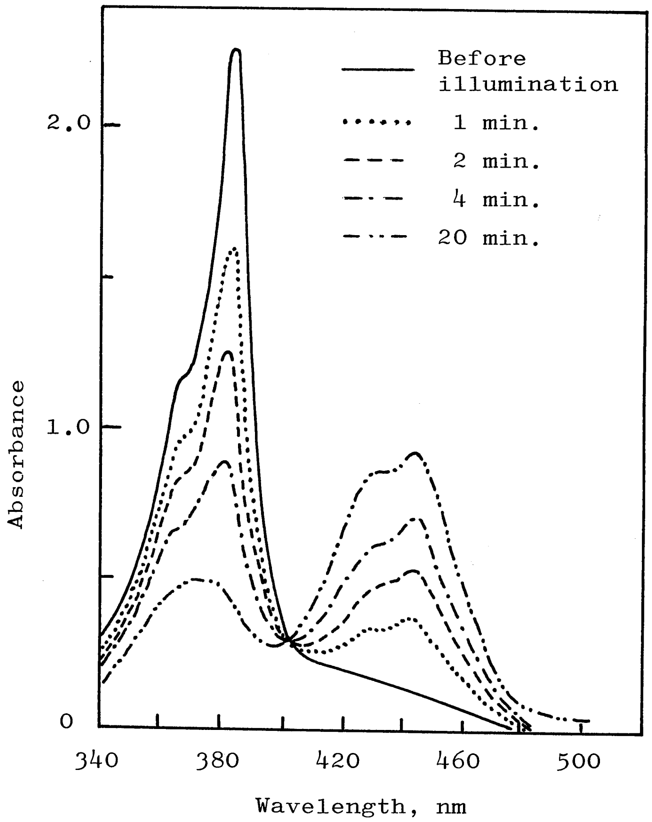


Fig. 1. The absorption spectral change of the PH$^+$ in aqueous sulfuric acid solution (0.97 x 10^{4} mol/l, pH 0.17) with the illumination time.

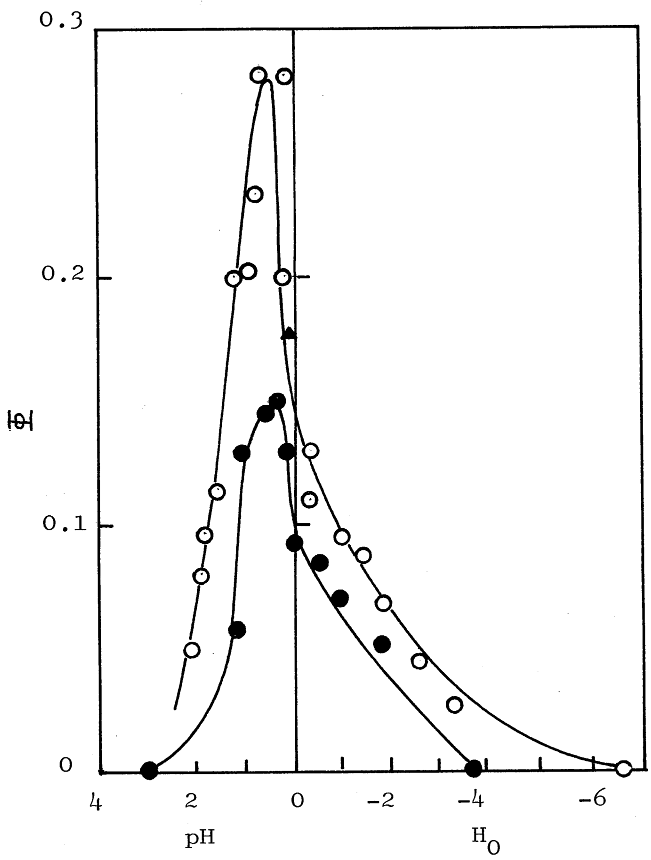


Fig. 2. The acidity dependence of the quantum yield for disapperance of PH$^+$, Φ.

—○— in the aerated solution, —●— in the deaerated solution.

and ESR spectra with those of literature.1,3,4) It should be noticed that no ESR signal due to the 1-hydroxydihydrophenazine cation radical was observed.

Acidity dependence of the quantum yield for disappearance of PH^+, Φ, was examined in the aerated and the deaerated aqueous sulfuric acid solutions. In order to obtain Φ, the following equation5) derived for such a system that the photoproduct absorbs the exciting light to some extent was used;

$$\ln(e^{2.303A} - 1) - \ln(e^{2.303A_0} - 1) = 2.303 \times 10^3 \Phi I_0 \varepsilon \left[t - \varepsilon' C_0 \int_0^t (1/A) dt \right] \qquad (1)$$

where I_0, ε and ε' are the incident light intensity (mol/cm^2·s), molar extinction coefficients of PH^+ and the photoproduct at 365 nm, respectively. A_0 and A are absorbances of the samples before and during illumination, respectively. The results are given in Fig. 2. In both the aerated and the deaerated solutions, the increase in the yield at pH between 2.5 and 0.5 with decreasing pH is merely apparent due to the protolytic equilibrium in the ground state. At pH $<$ 0.5 and H_0 between 0 and -0.5, the yield decreases and falls to nil as pH or H_0 decreases. This decreasing curve at the right-hand side in Fig. 2 does not reflect pKa^{II}(-4.30 6)) at all. This lowering in Φ may be due to the decrease in the amount of water in the medium or to the suppression of the photoreaction process by the protonation process [I] in the excited singlet state.

$$PH^{+*} + H_3O^+ \longrightarrow PH_2^{2+*} + H_2O \qquad [I]$$

The relative fluorescence yield, Φ_{rf}, of the aerated solutions are plotted in Fig. 3 as a function of acidity. The relative yield of fluorescence and of the photochemical reaction are very similar and probably identical within the error, implying that the lowering in Φ is due to the occurence of the process [I].

It was established for the aerated solution at pH 1.05 that Φ is proportional to light intensity, biphotonic process being not involved within the light intensity of 2×10^{-9} mol /cm^2·s.

The detection of hydrogen peroxide, which is a possible by-product of this photoreaction, was attempted by the potassium hexacyanoferrate(III)-iron(III) ammonium sulfate method7) for the deaerated solution at pH 1.05. Its formation was confirmed by the color change of the test solution from red to dark green.

The effect of oxygen concentration on Φ was investigated in detail. A typical example at pH 0.5 is shown in Fig. 4. The minimum in the Φ vs. $[O_2]$ curve at $[O_2] \approx 6 \times 10^{-5}$M appears for solutions at different pH. This curve suggests the presence of two kinds of intermediates attacked by oxygen, one having a retarding effect and the

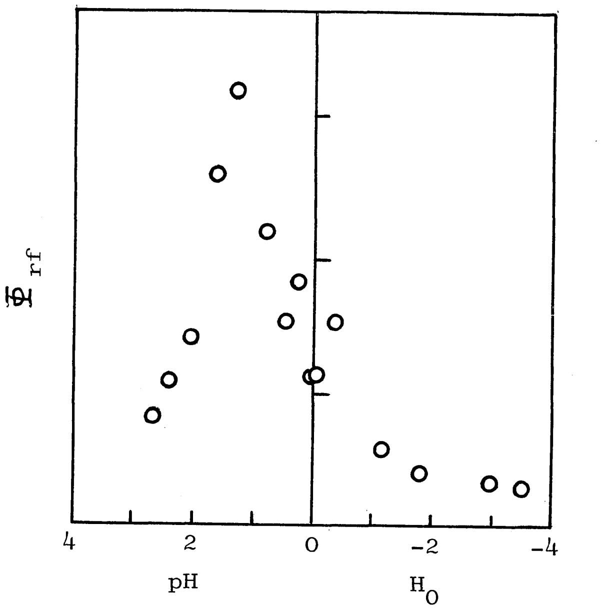


Fig. 3. The acidity dependence of the relative fluorescence yield, Φ_{rf}, of the aerated solutions.

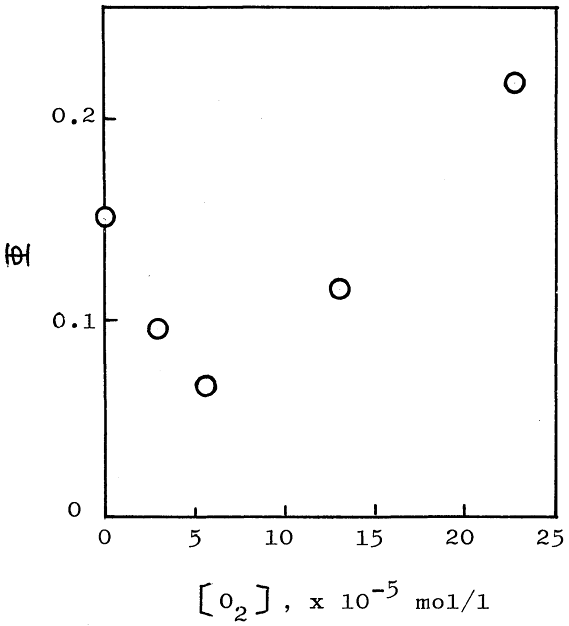


Fig. 4. The oxygen concentration effect on Φ.
$PH^+ = 8.6 \times 10^{-5}$ mol/l, pH 0.5.

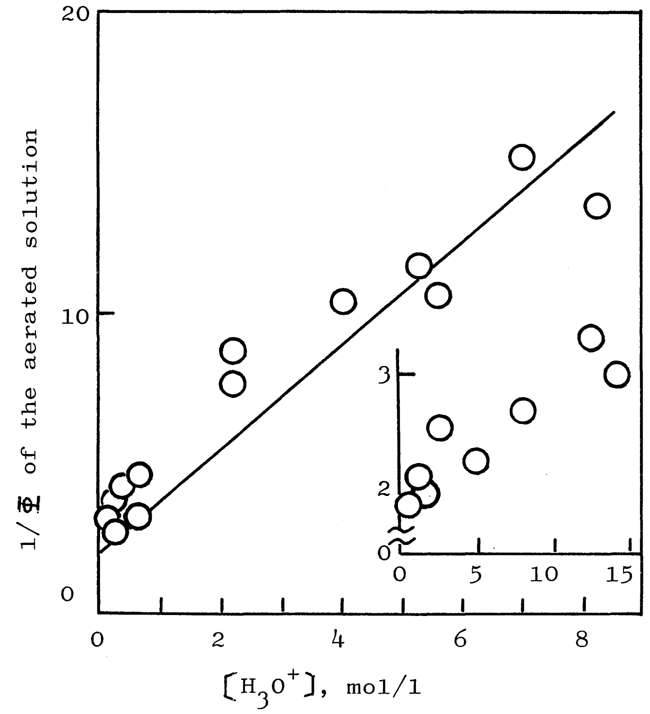


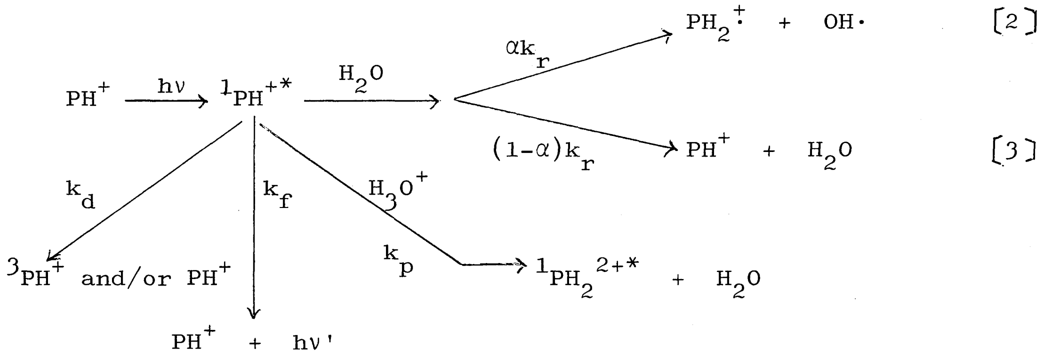
Fig. 5. The plot of the equation (2) in the text.

other a promoting effect on the overall reaction.

1,2-Dibromoethane added to the deaerated system as a $^3(\pi\pi^*)$ state quencher$^{1)}$ has no effect on Φ. Consequently, $^3(\pi\pi^*)$ state is confirmed not to take part in the reaction.

The color of the aerated, illuminated solution turns from lime green to reddish orange upon keeping the solution in the dark. The product was identified as 1-hydroxyphenazine by mass spectrometry and the absorption spectra (the absorption maximum at 500 nm in acidic, 520 nm in alkaline). In the deareated solution, however, $PH_2^{+\cdot}$ undergoes no dark reaction. The addition of an oxidizing agent such as potassium hexacyanoferrate(III) causes the formation of 1-hydroxyphenazine. To eliminate the possible reaction with by-product, the solvent was renewed before the addition of the oxidizing reagent, so that the hydroxy oxygen atom should be considered to come from the solvent water.

On the basis of the results obtained above, we propose the following scheme;



$$2OH\cdot \longrightarrow H_2O_2$$

where k's are the rate constants, α the efficiency of the reaction. It is obvious from the Φ vs. $[O_2]$ curve that processes [2] and [3] are not elementary ones. Then the following equations are readily derived.

$$\frac{1}{\Phi} = \frac{k_f + k_d + k_r[H_2O]}{\alpha\, k_r[H_2O]} + \frac{k_p}{\alpha\, k_r[H_2O]}[H_3O^+] \qquad (2)$$

$$\frac{1}{\Phi_{rf}} = \frac{k_p[H_3O^+]}{k_f + k_d + k_r[H_2O]} \qquad (3)$$

$1/\Phi$ and $1/\Phi_{rf}$ were plotted against $[H_3O^+]$. Two linear relations were obtained as shown in Figs. 5 and 6. The limitting Φ value for the air saturated system was determined to be 0.5 from the intercept of a straight line. The result also gave

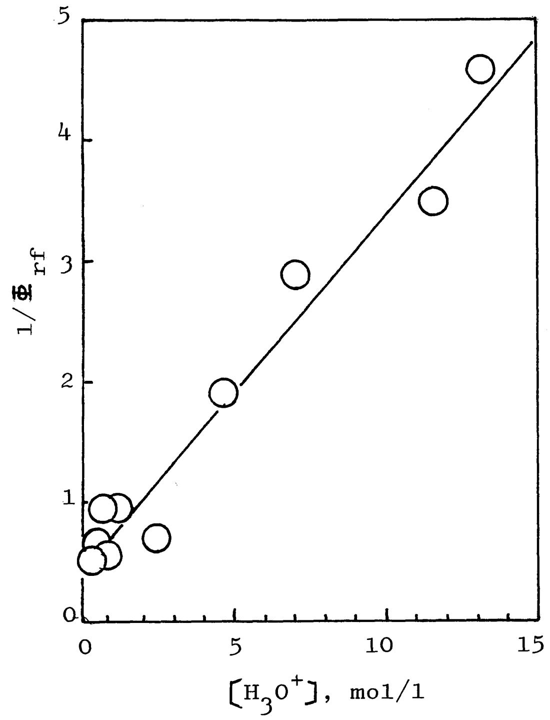


Fig. 6. The plot of the equation (3) in the text.

the restriction on α value; $1 \geqq \alpha \geqq 0.5$. For the deaerated system, 0.28 was obtained as the same quantity. On the other hand, from the intercept and the slope of the straight line given by the plot of $1/\Phi$ vs. $1/[O_2]$ using three measured points at higher oxygen concentration in Fig. 4, $\sim 1 \times 10^{-6}$s was estimated as the lifetime of one of the conceivable intermediates in processes [2] and [3], provided that this intermediate is attacked by oxygen with the diffusion controlled process. The lifetime of the other intermediate was estimated to be $\sim 3 \times 10^{-5}$s from the oxygen concentration where the effect of oxygen on Φ becomes detectable.

Details will be published elsewhere.

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