Effect of the pH Value on the Rate of the Photoreduction of Methylene Blue by N-Phenylglycines

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In the preceding paper, a preliminary result was described as to the dependence of the initial quantum yield, Φ, of the photoreduction of methylene blue by *N*-phenylglycines on the pH value of the medium. As Φ does not vary linearly with the concentration of electron donors, it is not sufficient to investigate the problem only at a definite electron donor concentration. The ionization of the *N*-phenylglycines is another factor to be studied. Moreover, Φ will also depend on the nature and concentrations of the buffer solutions. It is the object of this paper to investigate these factors in some detail.

Experimental

The photobleaching apparatus and the experimental method were the same as those described in the preceding paper. A Shimadzu Glass Electrode Potentiometric Titrator PT-1 was used to measure the pH value of solutions. Reagents for the buffer solutions were obtained from the Kanto Chem. Co., Inc. The phosphates were of the G. R. grade "for pH determination," while the others were of E. P. grades. The borax was recrystallized once from water. Corrections for ionic strength were made with sodium chloride which was also a G. R. reagent from the Kanto Chem. Co., Inc.

Results and Discussion

1.—First, two orienting experiments were carried out.

a. Dissociation of N-Phenylglycines.—Figure 1 shows the titration curve of *N*-phenylglycine (10^{-2} mol./l.) with a 0.0553 N sodium hydroxide solution. The points agree fairly well with the calculated curve for monobasic acid of pK_a 4.3, except in alkaline regions, where the deviation is probably due to the effect of atmospheric carbon dioxide. It is evident, therefore, that *N*-phenylglycine exists only in a definite form, $C_6H_5NH\cdot CH_2\cdot COO^-$, in aqueous solutions with pH values within the 5.9~10.5 range, where the experiments were performed. Such other forms as $C_6H_5NH\cdot CH_2\cdot COOH$ and $C_6H_5NH_2{}^+\cdot CH_2\cdot COO^-$ may be neglected in this study. Similar experiments gave the pK_a values of various *N*-phenylglycines; these are listed in Table I.

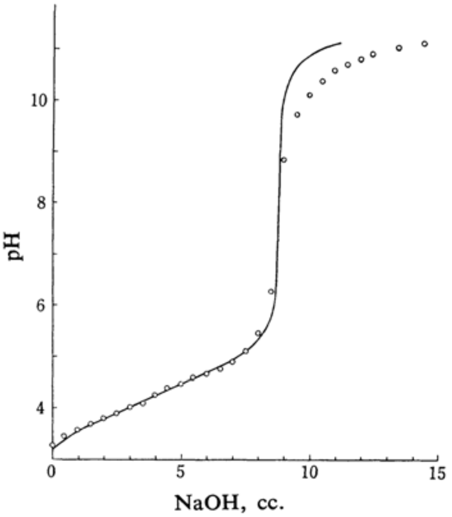

Fig. 1. Base titration of *N*-phenylglycine.

TABLE I. pK_a OF SUBSTITUTED *N*-PHENYLGLYCINES

$\phi\cdot$G	*p*-Cl-$\phi\cdot$G	*p*-CH$_3$-$\phi\cdot$G
4.3	3.9	5.0
p-CN-$\phi\cdot$G	*p*-Ac-$\phi\cdot$G	*m*-COOH-$\phi\cdot$G
3.8	3.7	(3.7)*

* The pH of half titrated soln. Ionization of the two COOH-groups cannot be separated titrimetrically.

b. Effect of the Concentration of Buffer Solutions and Ionic Strength. — The quantum yield, Φ, of the photoreduction was measured in buffer solutions of three different concentrations at various pH values. The ionic strength, μ, was designed to be constant. The results are shown in Fig. 2, which clearly shows the effect of buffer concentration. It is

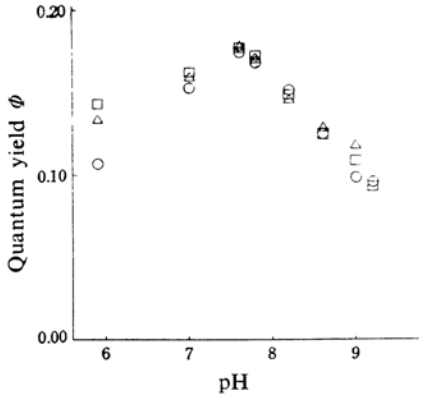

Fig. 2. Effect of buffer concentration on Φ.
Electr. donor p-Cl-$\phi\cdot$G 1.0×10^{-4},
M. B. 2.5×10^{-6} M

Buff. concn., mol./l.

pH	5.9*	7.0*	7.8*	7.6†
○	0.102	0.056	0.044	0.088
△	0.061	0.033	0.026	0.053
□	0.020	0.011	0.009	0.018
pH	**8.2†**	**8.6†**	**9.0†**	**9.2†**
○	0.097	0.109	0.131	0.140
△	0.058	0.065	0.078	
□	0.019	0.022	0.026	0.028

* KH_2PO_4-Na_2HPO_4 buff. $\mu=0.122$ g. ion./l.
† $Na_2B_4O_7$-HCl buff. $\mu=0.071$ g. ion./l.

TABLE II. EFFECT OF IONIC STRENGTH ON Φ

μ (g. ion./l.)	0.049	0.074	0.149	0.449
Φ	0.159	0.162	0.144	0.139

especially marked at the lower end of the pH region. The effect of ionic strength at a constant buffer concentration is shown in Table II. It is seen that the effect is within the range of experimental error for $\mu<0.1$ g. ion/l.

To avoid the above complexity, it would be best, theoretically, to use the Φ's extraporated to those in infinitely dilute buffer solutions. However, this procedure would be too troublesome to be practicable, and the errors in the extrapolation might be appreciable. Accordingly, the following experiments were performed in buffer solutions in which the total phosphate, borate or carbonate concentration and the ionic strength were maintained at constant and minimum practical values.

2. Dependence of Φ_∞, $1/b$ and B on pH Value. —At every pH value the following relation¹⁾ holds:

$$1/\Phi=1/\Phi_\infty+b/[\mathrm{E}]$$

where [E] is the concentration of the electron donor and Φ_∞ and b are constants for the particular conditions. Φ_∞ and b naturally

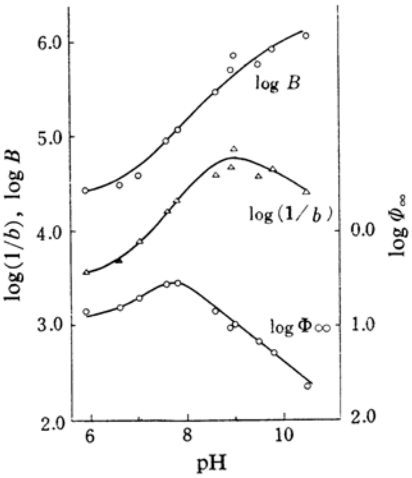

Fig. 3. Dependence of Φ_∞, $1/b$ and B on pH.
Electr. donor p-Cl-$\phi\cdot$G M. B. 2.5×10^{-6} M
40°C

depend on the pH value. In Fig. 3 their values and the $B=1/(\Phi_\infty\cdot b)$ value¹⁾ for N-p-chlorophenylglycine are plotted on a logarithmic scale against the pH values. The dependence of Φ_∞ on the pH value is similar to that of Φ measured at a definite electron donor concentration. This is in contrast to Oster's²⁾ results with EDTA, where Φ_∞ was independent of the pH value. On the other hand, $\log(1/b)$ and $\log B$ increase markedly with an increase in the pH value. Log B increases especially steadily and is linear with the pH value in the 7∼9 range³⁾. The slope is approximately 0.51. Figure 4 shows similar results with N-phenylglycine. In this case, the variation of Φ_∞ is smaller, but the slope of $\log B$ against the pH value is nearly the same. Figure 5 shows the results with N-p-acetylphenylglycine, which has a much smaller reactivity¹⁾ than the above two N-phenylglycines. The slope of $\log B$ is approximately 0.45.

To see whether the linear dependence of $\log B$ on the pH value is a general occurrence, it is desirable to investigate also with other simple molecules. Methylamines are the simplest, but their dissociation constants are comparatively large, and for the study with uniform ionic species⁴⁾, the bleaching must be measured in a region of higher pH value,

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1) Cf. (the preceding paper) S. Matsumoto, 35, 1860 (1962).

2) G. Oster and N. Wotherspoon, *J. Am. Chem. Soc.*, 79, 4836 (1957).

3) At higher pH values, the photobleaching of methylene blue occurs appreciably in the absence of any reductant, and rigorous treatment of the data is more difficult, unless the nature of such bleaching is definitely established, than at a low pH value where the photobleaching is negligible in the absence of a reductant. In the above calculation of Φ, such a bleaching rate was merely subtracted, for the moment, as 'blanck' from the total bleaching rate.

4) Cf. section 1, a of this paper.

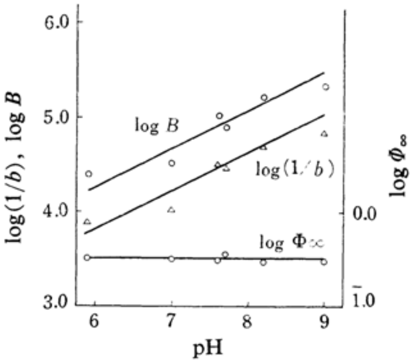


Fig. 4. Dependence of Φ_∞, $1/b$ and B on pH. Electr. donor $\phi\cdot$G M. B. 2.5×10^{-6} M 40°C

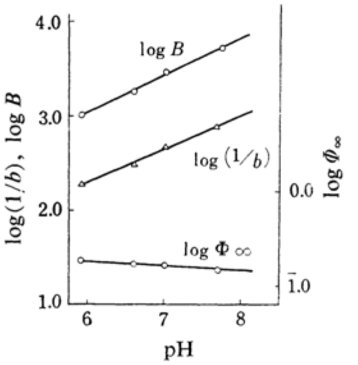


Fig. 5. Dependence of Φ_∞, $1/b$ and B on pH. Electr. donor p-Ac-$\phi\cdot$G M. B. 2.5×10^{-6} M 40°C

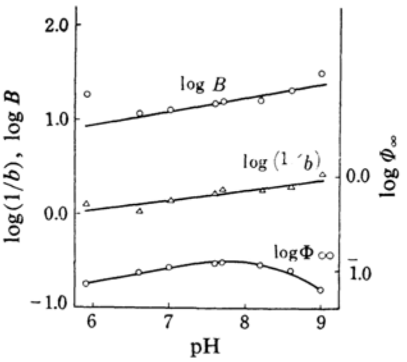
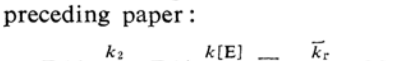


Fig. 6. Dependence of Φ_∞, $1/b$ and B on pH. Electr. donor $NH_2\cdot CO\cdot NH\cdot NH_2$ M. B. 2.5×10^{-6} M 40°C

where another complexity arises[3]. Among the several substances tested, semicarbazide was found to have ability as a photoreductant and also to have a low ionization constant: $pK_b=10.6$[5]. Its effectiveness was, however, very much smaller than that of the N-phenylglycines. The results are shown in Fig. 6. It is interesting that the pH value dependences of Φ_∞, $1/b$ and B are similar for this different kind of substance. The slope of $\log B$ against the pH value is, however, much smaller (ca. 0.1) than those in the preceding cases.

Let the following scheme be assumed as in the preceding paper:



Then,

$$\Phi=\varphi\cdot\gamma_E\{k[E]/(k_s+k[E])\}\{\overline{k}_r/(\overline{k}_d+\overline{k}_r)\}$$

$$\Phi_\infty=\varphi\cdot\gamma_E\cdot\overline{k}_r/(\overline{k}_d+\overline{k}_r)$$

$$1/b=\varphi\cdot\gamma_E(k/k_s)\{\overline{k}_r/(\overline{k}_d+\overline{k}_r)\}$$

and $$B=k/k_s$$

The simpler dependence of B is in accord with the simpler expression of B than those of Φ_∞ and $1/b$.

If k_s is independent of the pH value, then

$$\partial \log B/\partial \mathrm{pH}=\partial \log k/\partial \mathrm{pH}$$

In most of the cases described above, this slope is approximately 0.5, so that $k\propto\sqrt{[OH^-]}$. This may suggest the contribution of OH^- in the reaction: $D^{+t}+E\rightarrow\overline{M}$, though the true nature is uncertain as yet.

Summary

The effect of the pH value on the rate of the photoreduction of methylene blue by N-phenylglycines was studied in detail in the range between 5.9 and 10.5, attention being paid to the effects of buffer solutions and to a possible change in the ionic species of N-phenylglycines with the change in pH value. N-Phenylglycine behaved as a monobasic acid of pK_a 4.3 to base titration, so that it existed solely as a univalent anion $C_6H_5NH\cdot CH_2COO^-$ in this pH value range. The pK_a of several other N-phenylglycines was given also. The concentration and ionic strength of the buffer solutions had some effect; they must be kept constant and as small as possible.

With these precautions, the pH value dependences of Φ_∞, $1/b$ and $B=1/(\Phi_\infty\cdot b)$, which characterize the quantum yield of the photoreduction, were determined for several electron donors. They were similar in all cases. Semicarbazide was found to be effective as an electron donor for this photoreduction. Log B varied linearly with the pH value in the pH range between 7.0 and 9.0. The slopes were nearly 0.5 for all the N-phenylglycines studied. This means that, if the excited metastable state of the dye formed a complex before the oxidation-reduction reaction, the rate constant of

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[5] N. A. Lange, "Handbook of Chemistry", 8th Ed., Handbook Publishers, Inc., Sandusky, Ohio (1952), p. 1235.

its formation must vary as the root of the hydroxide ion concentration.

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