Photoreduction of Methylene Blue by Some Derivatives of N-Phenylglycine. Relation between the Structure and the Reactivity of the Electron Donors

By Shiro MATSUMOTO

(Received July 11, 1962)

It has been reported[1] that the photoreduction of methylene blue was effected in deaerated solutions by some chelating agents, including *N*-phenylglycine. To elucidate the mechanism of the photoreduction of dyestuffs and to understand, in general, the nature of the reactions of photo-excited species, it may be useful to investigate systematically the effects of changes in the structure of the reducing agent (the electron donor). *N*-Phenylglycine was chosen as a suitable starting material for this purpose, as its homologues and benzene ring-substituted derivatives are well characterized (loc. cit.) and are prepared easily in a fairly good crystalline state.

N-Phenylglycine becomes unstable to air-oxidation upon the introduction of electropositive substituents into the ortho- and para-positions of the benzene ring, while the introduction of electronegative substituents has the opposite effect. A solution of *N*-*p*-oxyphenylglycine soon assumes a brown color, especially when it is alkaline, while *N*-*p*-nitrophenylglycine can be heated in boiling water without any appreciable decomposition. It seems, therefore, that the rate of the photoreduction of the dyestuff in the presence of various benzene ring-substituted *N*-phenylglycines should increase in proportion to the order of the electron-repelling tendency of the substituents. The highest rate was observed, however, with unsubstituted *N*-phenylglycine. Both positive and negative substituents reduced the efficiency of the *N*-phenylglycine as a photoreductant.

This apparent contradiction can be explained by taking into account the possibility of the deactivation of the excited dye ions by the reductant ions. In fact, *N*-*p*-methoxyphenylglycine was found to have a remarkable retarding effect, comparable to that of *p*-phenylenediamine[1], upon the photoreduction of the dye by other reducing agents. It is shown in this paper that, if a customary reaction scheme is assumed, certain of its rate constants parallel Hammett's σ[2] value for the substituent.

Other kinds of derivatives of *N*-phenylglycine were also examined; it was found that the replacement of the hydrogen atom, either on the nitrogen or on the α-carbon atom of *N*-phenylglycine, by the methyl group did not deprive it of the ability to photoreduce the dye. These hydrogen atoms, therefore, do not take part in the photoreduction. On the other hand, the insertion of a methylene unit between the amino and the carboxyl group greatly reduced the ability.

Experimental

Benzene ring-substituted *N*-phenylglycines were prepared from the corresponding anilines either by the action of haloacetic acid or by Knoevenagel's[3] or Schwalbe's[4] method. *N*-Methyl-*N*-phenylglycine was prepared by the action of ethyl bromoacetate on dimethylaniline[5], followed by hydrolysis. It was separated as hydrochloride and purified in this form. α-Methyl-*N*-phenylalanine was prepared by the hydrolysis of the nitrile, which had been obtained by the action of potassium cyanide on the acetone in acetic acid[6]. *N*-Acetyl-*N*-phenylglycine was prepared by the acetylation of *N*-phenylglycine with acetic anhydride[7]. *N*-phenyl-β-alanine was prepared by the action of 3-bromopropanoic acid on aniline[8].

Methylene blue was a G. R. grade reagent from the Koso Chem. Co. and was used without further purification. Its molar extinction coefficient at 665 mμ was 8.16×10^4. *p*-Phenylenediamine hydrochloride was a G. R. grade reagent from the Kanto Chem. Co.

Photobleaching was followed, in an apparatus which was similar to that used by Pestemer[9], by some practical modification. The light source for the reaction was a 200 W./100 V. incandescent lamp operated at 78 V. This voltage was regulated to within 0.03 V. during a run. The light, filtered through a layer of water and an interference filter ($\lambda_{\max}$. 665 mμ, band width 12 mμ), fell on a reaction

---

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

[2] L. P. Hammett, "Physical Organic Chemistry", McGraw-Hill Book Co., New York, N. Y. (1940), Chap. 7.

[3] E. Knoevenagel, *Ber.*, **37**. 4065 (1904).

[4] C. G. Schwalbe, W. Schulz and H. Jochheim, ibid., **41**, 3790 (1908).

[5] J. F. Thorpe and A. S. Wood, *J. Chem. Soc.*, **103**, 1601 (1913).

[6] R. v. Walther and R. Hübner, *J. prak. Chem.*, [2] **93**, 119 (1916).

[7] C. A. Bischoff and A. Hausdörfer, *Ber.*, **25**, 2270 (1892).

[8] C. A. Bischoff and N. Mintz, ibid., **25**, 2345 (1892).

[9] M. Pestemer, *Z. Elektrochem.*, **58**, 121 (1954).

cell in a thermostat kept to 40±0.1°C. The transmitted light was measured by a photocell to follow the change in the optical density. The thickness of the liquid layer was 15.5 mm., while the light intensity was estimated to be 2.2×10^{14} photons per cm^2 per sec. A metal net was inserted between the light source and the cell to reduce the light intensity if necessary. Deaeration was achieved by flushing with nitrogen as in Pestemer's[9] experiment.

Absorption spectra and total fluorescence intensity were measured by a Shimadzu Spectrophotometer QR 50.

Results and Discussion

A qualitative test showed that *N-p*-chlorophenylglycine (p-Cl-$\phi\cdot$G) would be more suitable than unsubstituted *N*-phenylglycine ($\phi\cdot$G) as a reference substance. The former was found to be more stable in air, though it caused the photobleaching nearly as effectively as the latter. Therefore, all the preliminary experiments to inspect various factors were performed with this substance as the electron donor.

1. Time Course of the Bleaching.—The change in the optical density, *D*, with time could be expressed quite well by the superposition of two exponential terms, as in the case of methylamines reported by Obata and Koizumi[10]. An example is shown in Fig. 1, in which the curve is drawn according to $D=0.1099\times10^{-0.00344t}+0.0220\times10^{-0.000787t}$. This fact may be explained most simply by assuming an intermediate that slowly accumulates during the course of the reaction[10]. However, to avoid complexity in treating the kinetic data and to minimize special assumptions, it may be convenient to consider, for the moment, only the early stage of the photoreduction. At this stage, such intermediates, if any, can safely be neglected. Therefore, Bodenstein's stationary state method may be used to derive the rate equation. Accordingly, tangents were drawn at time zero to the log *D* versus time curves, which were usually convex to an ordinate showing the deviations from the first order kinetics; the initial values of quautum yield Φ[11] were calculated from the slopes.

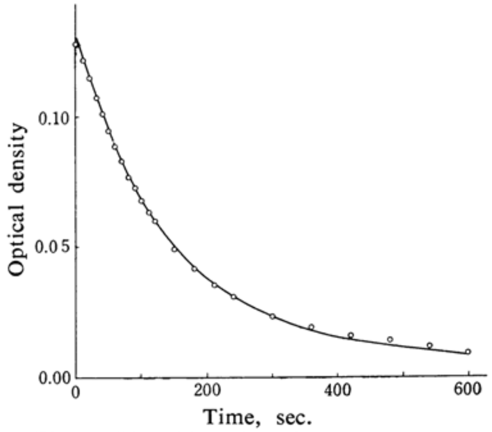


Fig. 1. Photobleaching of M.B.
M.B. 1.1×10^{-6} M, p-Cl-$\phi\cdot$G 1.0×10^{-4} M
pH 7.0 40°C

2. Effect of Light Intensity on Φ.—As is shown in Table I, a two-to three-fold variation in light intensity has little effect on Φ.

TABLE I. EFFECT OF LIGHT INTENSITY ON ϕ
M.B. 1.5×10^{-6} M, p-Cl-$\phi\cdot$G 1.0×10^{4} M pH 7.0

Relative intens.*	1.00	0.55	0.34
Φ	0.150	0.157	0.147

* Stand. intens. 2.2×10^{14} photons/cm$^2\cdot$sec.

3. Effect of Dye Concentration.—Table II shows that Φ is practically independent of the dye concentration in the $(1\sim5)\times10^{-6}$ mol./l. range.

TABLE II. EFFECT OF DYE CONCN. ON Φ
p-Cl-$\phi\cdot$G 1.0×10^{-4} M. pH 7.0

Dye concn. $\times10^6$ M	0.92	1.53	3.13	5.47
Φ	0.141	0.150	0.150	0.130

4. Effect of the pH Value.—The points in Fig. 2 are taken from some preliminary experiments, where the concentrations of the methylene blue and p-Cl-$\phi\cdot$G were fixed arbitrarily at 1.5×10^{-6} and 1.0×10^{-4} mol./l. respectively. A maximum is observed at a pH value near 7.8. However, Φ depends also on the concentration of the electron donor. This matter will be described more fully in the next paper, together with the effect of buffer solutions.

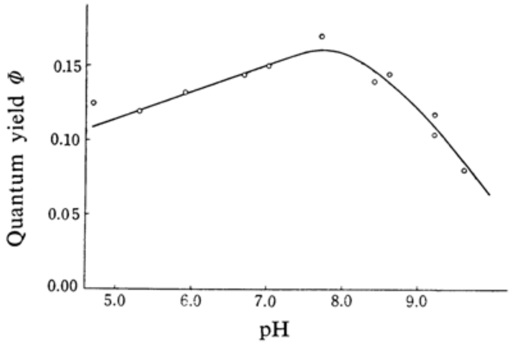


Fig. 2. pH dependence of quantum yield.
M. B. 1.5×10^{-6} M, p-Cl-$\phi\cdot$G 1.0×10^{-4} M 40°C

---

10) H. Obata and M. Koizumi, This. Bulletin, 30, 136, 142 (1957).

11) Any inaccuracy in the determination of the absolute light intensity does affect the absolute values of Φ, but their relative values are of main interest here.

5. Dependence of Φ on the Concentration of the Electron Donor.—The dependence is expressed by the equation:

$$1/\Phi = 1/\Phi_0 + b/[\mathrm{E}] \qquad (1)$$

where Φ_0 and b are constants and [E] is the concentration of the electron donor. An example is shown in Fig. 3.

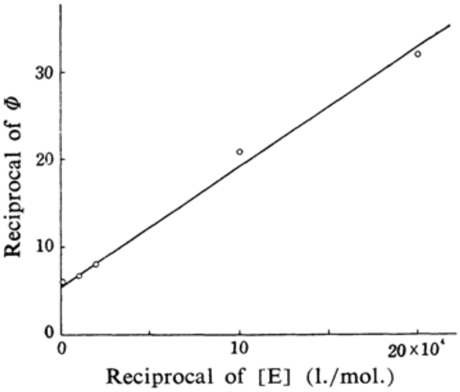


Fig. 3. Dependence of Φ on electron donor concn.
E: p-Cl-$\phi\cdot$G, pH 7.0 40°C

6. Dependence of Φ on the Structure of the Electron Donor.—In Table III are summarized the Φ's of the photoreduction by various N-phenylglycines and related compounds of the same molarity (10^{-4} mol./l. except for N-phenyl-β-alanine, for which 10^{-3} mol./l.). It is seen that the replacement of the hydrogen atom on the nitrogen or α-carbon atom of N-phenylglycine by a methyl group does not deprive it of its ability as a photoreductant. These hydrogen atoms are therefore, not included in photoreduction process; and reduction is probably initiated by electron transfer from the reducing ions to the excited dye cations. N-Acetylation reduces the ability, but this may be due either to steric effects or to the electron-attracting influence of the acetyl group (see below). The insertion of a methylene unit between the amino and the carboxyl group greatly reduces the ability as a photoreductant.

Table III also shows that both electropositive and electronegative substituents in the ortho- and para-positions reduce the effectiveness of the N-phenylglycine. Moreover, bromine-substitution in these positions has a much more pronounced effect than chlorine-substitution, though these two elements have nearly the same substituent effects in ordinary thermal reactions, as is seen in their similar Hammett σ[2] values. It may be added here that slow bleaching is observed even in the absence of any reducing agent (the quantum yield is of the order of 10^{-3} at a pH value of 7). Such slow bleaching is completely absent in the presence of N-p-methoxyphenylglycine (p-MeO-$\phi\cdot$G), while it is at least preserved in the case of N-p-nitrophenylglycine (p-NO_2-$\phi\cdot$G). These facts suggest the parallel occurrence of the retardation by the reductants themselves. It is also interesting that the effect of substituents is much smaller in meta-substitution than in ortho- and para-substitutions. It is especially ramarkable that N-m-methoxyphenylglycine (m-MeO-$\phi\cdot$G) normally photoreduces the dye.

In regard to the high efficiencies of N-phenylglycines in the photoreduction, a question arises whether any complex is formed between N-phenylglycines and the dye in its ground state, the complex being ready to undertake inner oxidation-reduction upon the absorption of light. To check this point, the absorption spectra of the reaction mixtures were examined, together with those of the components from the ultraviolet end to the red end of the

TABLE III. INITIAL QUANTUM YIELD Φ OF PHOTOREDUCTIONS BY VARIOUS DERIVATIVES OF N-PHENYLGLYCINE

M. B. 1.5×10^{-6} M, $\phi\cdot$G's 1.0×10^{-4} M pH 7.0

a) Benzene ring-substituted N-phenylglycines

Substituent	HO	MeO	Me	H	Cl	Br	COOH	MeCO	CN	NO_2
ortho	0.000	0.003			0.092	0.018				0.001
Position meta		0.169		0.230	0.147	0.063	0.167			0.022
para	0.000	0.000	0.076		0.150	0.010		0.041	0.010	0.001

b) Other derivatives

$\phi N(CH_3)\cdot CH_2\cdot COOH$	0.235	$\phi N(COCH_3)\cdot CH_2\cdot COOH$	0.003
$\phi NH\cdot C(CH_3)_2\cdot COOH$	0.305	$\phi NH\cdot (CH_2)_2\cdot COOH$†	0.009

† 10^{-3} M

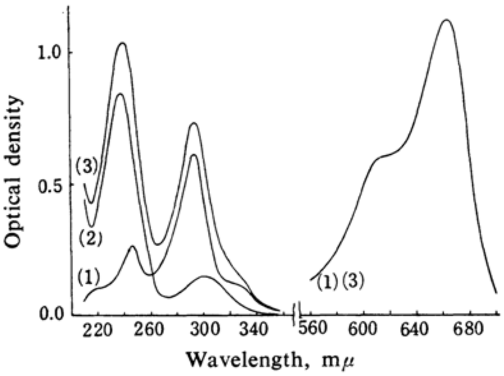


Fig. 4. Absorption curves of solns. of M. B., *p*-MeO-$\phi \cdot$G and their mixture. (1) M. B. 1.44×10^{-5} M (2) *p*-MeO-$\phi \cdot$G 7.65×10^{-5} M (3) M. B. 1.44×10^{-5} M, *p*-MeO-$\phi \cdot$G 7.65×10^{-5} M pH 7.0. In the visible region, where the $\phi \cdot$G does not absorb, curve (3) coinsides with (1).

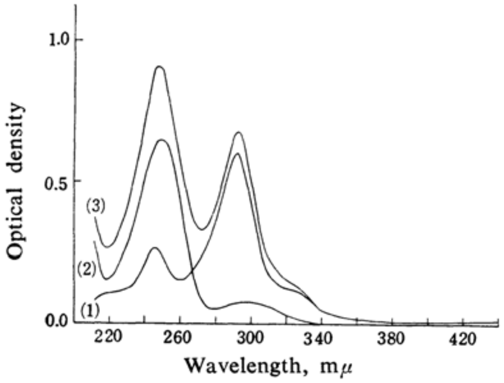


Fig. 5. Absorption curves of solns. of M. B., *p*-Cl-$\phi \cdot$G and their mixture. (1) M. B. 1.44×10^{-5} M (2) *p*-Cl-$\phi \cdot$G 4.92×10^{-5} M (3) M. B. 1.44×10^{-5} M, *p*-Cl-$\phi \cdot$G 4.92×10^{-5} pH 7.0. Absorption in longer-wavelength region is the same as that in Fig. 4.

visible region. As may be seen in Figs. 4 and 5, a good additivity holds in the entire region. No sign of complex formation is observed.

The following scheme may tentatively be assumed as the simplest for describing the reaction sequences:

$$\begin{tikzcd}
D^{+*} \arrow[r, "k_2"] \arrow[d, shift left, "k_1"] & D^{+t} \arrow[r, "k_r\text{[E]}"] \arrow[dl, "k_s+k_d\text{[E]}"] & M \arrow[r] \arrow[dl, "\gamma_E"'] & \text{Red. Prod.} \\
D^{+} \arrow[u, shift left, "h\nu"] & &
\end{tikzcd}$$

where D^+ is the dye cation in the ground state, and D^{+*} is that in its first electronically-excited singlet state. A second metastable excited state, D^{+t}, is assumed for the same reason as in some other cases[9,12]. It was confirmed that the fluorescence intensity of methylene blue was little affected by the addition of *p*-Cl-$\phi \cdot$G or *p*-MeO-$\phi \cdot$G up to a concentration of 10^{-4} mol./l.

The rate constants of deactivation, k_1 and k_s, may contain terms that correspond to the deactivation by the emission of radiation, as well as terms corresponding to radiationless deactivation. The deactivation of D^{+t} must be enhanced by E (an electron donor), as is stated above, which is represented by the term, k_d[E]. Adding a term representing the deactivation of D^{+*} by E is not justifiable because that will lead to a rate equation that has not the simple form of Eq. 1. The reduction of D^{+t} may take place via intermediate, M, some fraction of which may foil to give the reduction product. The fraction of M's that succeeds in getting to the final product is denoted by γ_E.

Therefore, Φ may be expressed according to Bodenstein's approximation:

$$\Phi = \varphi \cdot \frac{k_r\,[\mathrm{E}]}{k_s + (k_d + k_r)\,[\mathrm{E}]} \cdot \gamma_E \tag{2}$$

where $\varphi = k_2/(k_1+k_2)$ may be said to be the quantum yield of the first stage. Equation 2 is identical with Eq. 1, if $\Phi_\infty = \varphi \cdot \gamma_E \cdot k_r/(k_d+k_r)$ and $1/b = \varphi\gamma_E \cdot k_r/k_s$. Φ_∞ is the quantum yield extrapolated for infinite electron

TABLE IV. Φ_∞ AND $1/b$ FOR VARIOUS ELECTRON DONORS

a) Benzene ring-substituted *N*-phenylglycines

Substituent	Φ_∞	$1/b$ (l./mol.)
p-MeO*		(0)
m-MeO	0.236	7.59×10^3
p-Me	0.077	1.73×10^4
H	0.274	1.17×10^4
o-Cl	0.206	1.64×10^3
m-Cl	0.260	3.57×10^3
p-Cl	0.185	7.39×10^3
o-Br	0.023	5.51×10^2
m-Br	0.087	2.04×10^3
p-Br	0.014	9.50×10^2
m-COOH	0.229	4.97×10^3
p-COMe	0.218	5.07×10^2
p-CN	0.227	1.07×10^2
m-NO_2	0.212	2.68×10^2
p-NO_2	0.05	6.7

b) Other derivatives

	Φ_∞	$1/b$ (l./mol.)
$\phi N(CH_3) \cdot CH_2 \cdot COOH$	0.278	2.71×10^4
$\phi N(COCH_3) \cdot CH_2 \cdot COOH$	0.039	4.99×10
$\phi NH \cdot C(CH_3)_2 \cdot COOH$	0.388	1.31×10^4
$\phi NH \cdot CH_2 \cdot CH_2 \cdot COOH$†	(0.032)	(1.40×10^2)

* $B = 1/(\Phi_\infty b) = 5.29 \times 10^5$ l./mol. † $B = 4.31 \times 10^3$ l./mol. These values and the values in ( ) were obtained from retardation experiments (section 7).

---

[12] G. Oster and A. H. Adelman, *J. Am. Chem. Soc.*, **78**, 913 (1956).

donor concentration and is naturally the Φ when k_s is neglected compared with (k_d+k_r) [E]. In this kinetic scheme, $1/b$ represents the relative effectiveness of $\phi\cdot$G's as a photoreductant, if k_s is independent of the nature of the added substances. These quantities can be obtained from plots similar to those in Fig. 3.

The results are summarized in Table IV. As is seen in the table, *o*- and *p*-Br-$\phi\cdot$G, for which unexpectedly small Φ values were observed, have small Φ_∞ values, which implies large k_d values.

7. Direct Measurement of the Retardation by *N*-Phenylglycines.—The retarding action of *N*-phenylglycines is demonstrated in the plots of Fig. 6, where Φ is measured in a system containing 1.5×10^{-6} mol./l. of methylene blue and 1.0×10^{-4} mol./l. of *p*-Cl-$\phi\cdot$G, to which are added various concentrations [E′] of retarding $\phi\cdot$G's. When $[E']=0$, the system bleaches with $\Phi=0.150$. Φ decreases, in general, by the addition of $\phi\cdot$G's, which were above suspected of retarding action. The effect of *p*-MeO-$\phi\cdot$G is most remarkable; it shows only a retarding action. The efficiency is comparable to that of the well-known retarder *p*-phenylenediamine (PPD)[1]. The retarding ratio $R_{\mathrm{ret}}=\Phi_0/\Phi$ (Φ_0 and Φ are the quantum yields in the absence and in the presence of retarders respectively) with 10^{-5} mol./l. of PPD was 1.88, whereas that with *p*-MeO-$\phi\cdot$G was 1.79. It is interesting that *p*-MeO-$\phi\cdot$G is isoelectronic with PPD. Other $\phi\cdot$G's, e. g., *p*-Br-$\phi\cdot$G, cause photobleaching by themselves. If it is assumed that these $\phi\cdot$G's compete with *p*-Cl-$\phi\cdot$G in reacting with D^{+t}, the equation for Φ is modified as follows:

$$\Phi=\varphi\cdot(\gamma_E\cdot k_r[E]+\gamma_E' k_r'[E'])/\{k_s+(k_d+k_r)[E]+(k_d'+k_r')[E']\}$$

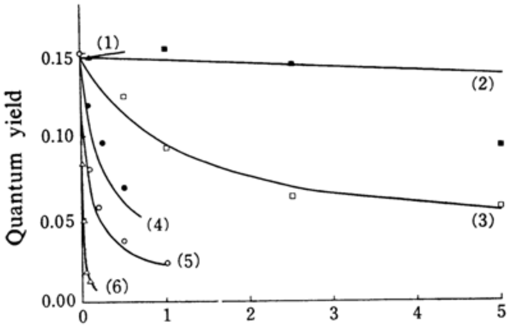


Fig. 6. Retardation by *N*-phenylglycines. Test soln. contains : *p*-Cl-$\phi\cdot$G 1.0×10^{-4} M, retdg. $\phi\cdot$G's [E′] M and M. B. 1.5×10^{-6} M pH 7.0 (1) *m*-NO$_2$-$\phi\cdot$G (2) *p*-NO$_2$-$\phi\cdot$G (3) *N*-ϕ-β-alanine (4) *o*-Br-$\phi\cdot$G (5) *p*-Br-$\phi\cdot$G (6) *p*-MeO-$\phi\cdot$G

where k_d', k_s' and γ_E' are the quantities corresponding to k_d, k_s and γ_E respectively for the second $\phi\cdot$G.

Or

$$\Phi=\varphi\cdot\frac{[E]/b+[E']/b'}{1+[E]/(b\cdot\Phi_\infty)+[E']/(b'\cdot\Phi_\infty')} \quad (3)$$

Again, b' and Φ_∞' correspond to b and Φ_∞ respectively. This relation could be checked by the insertion of the values of b, Φ_∞, b' and Φ_∞' given in Table IV. The curves in Fig. 6 are drawn to show this calculation. They coincide, at least qualitatively, with the experimental results. Φ_∞ and b could not be determined directly for *p*-MeO-$\phi\cdot$G and *N*-phenyl-β-alanine. In these cases, the insertion of the b and Φ_∞ values of *p*-Cl-$\phi\cdot$G into Eq. 3 gave:

$$\Phi=(0.739+A[E'])/(5.00+B[E'])$$

where $A=1/b'$ and $B=1/(b'\cdot\Phi_\infty')$. A and B were then determined, so that the best fit was obtained in Fig. 6. This required $B=5.29\times10^5$ and $A\fallingdotseq0$ for *p*-MeO-$\phi\cdot$G and $B=4.31\times10^3$ and $A=1.40\times10^2$ for *N*-phenyl-β-alanine respectively.

8. Reactivities of *N*-Phenylglycines and Hammett's σ Value.—The B quantity given above has a simpler kinetic meaning than either $1/b$ or Φ_∞ has; i. e., $B=1/(b\cdot\Phi_\infty)=(k_d+k_r)/k_s$. It is the sum of the rate constants for the reduction and deactivation of D^{+t} by the $\phi\cdot$G concerned, divided by the rate constant for the spontaneous deactivation. The value of k_s may be independent of the nature of the $\phi\cdot$G. Thus, B represents the relative total reactivity of the $\phi\cdot$G with D^{+t}.

Some relation might be sought between this value and Hammett's σ for the substituent in the benzene ring. The plots of $\log(B/B_0)$ versus σ are given in Fig. 7, where B_0 is the B

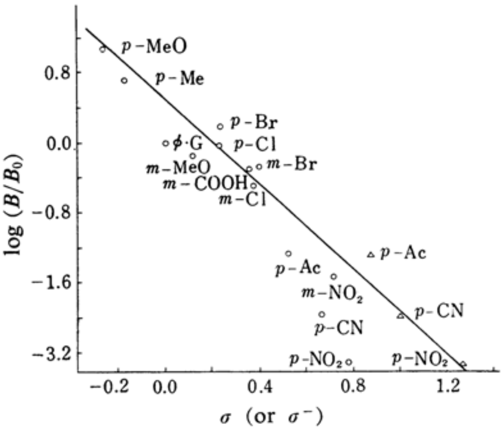
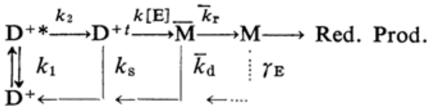


Fig. 7. Hammett's σ and the reactivity of *N*-phenylglycines.
○ : σ △ : σ^- pH 7.0 40°C

for the unsubstituted *N*-phenylglycine. It is seen that the points arrange near a straight line, the σ^- values giving better fits for the $+$E substituents. This might indicate the importance of the lone pair of electrons on the nitrogen atom of *N*-phenylglycine in the first stage of interaction with D^{+t} [13]. Although the detailed reason must be kept unspecified until other physico-chemical studies throw light from other angles on this problem, it is, nevertheless, interesting that a relation like Hammett's rule is found in a photochemical process.

The above considerations may be consistent with a kinetic scheme written in a more detailed form than the previous one:



where a step is imagined in which D^{+t} forms a loose complex, $\overline{M}$, with E before it is either reduced or deactivated by E. Then,

$$\Phi=\varphi\{k[E]/(k_s+k[E])\}\times\{\overline{k_r}/(\overline{k_d}+\overline{k_r})\}\ \gamma_E \tag{4}$$

and $k_d=k\cdot\overline{k_d}/(\overline{k_d}+\overline{k_r})$ and $k_r=k\cdot\overline{k_r}/(\overline{k_d}+\overline{k_r})$ correspond; i. e., Eq. 4 becomes identical with Eq. 2 with these substitutions. ***B*** becomes simply k/k_s, and the rate constant of the complex formation k bears a regular relation to δ irrespective of the $\overline{k}_r/\overline{k}_d$ ratio.

9. Evaluation of the Life-time of D^{+t}.— The retardation data with PPD may be used to estimate the lower limit of $1/k_s$, the life-time of the metastable state D^{+t}, using the method described by Oster and Adelman[12], in which it is assumed that the reaction is diffusion-controlled and that every collision of a PPD molecule with D^{+t} effectively deactivates the latter. It is easy to derive

$$R_{\text{ret}}=\Phi_0/\Phi=1+\frac{k_q/k_s}{1+\{(k_d+k_r)/k_s\}[E]}\cdot[X] \tag{5}$$

where X represents PPD or another quencher molecule and [X] is its concentration. The rate of the deactivation of D^{+t} is supposed to increase by a term of $k_q[X]$. Φ_0 is the Φ when $[X]=0$. As is stated above, $R_{\text{ret}}=1.88$ for $[X]=10^{-5}$ mol./l. and $[p\text{-Cl-}\phi\cdot G]=10^{-4}$ mol./l. As $(k_d+k_r)/k_s=1/(b\cdot\Phi_\infty)=4.00\times10^4$ l./mol. for p-Cl-$\phi\cdot$G (Table IV), Eq. 5 gives $k_q/k_s=4.4\times10^5$ l./mol. The number of collisions of a D^{+t} with X molecules in a unit of time is given as $(8\boldsymbol{R}T/3\eta)\cdot[X]\times10^{-3}$ [12] by the use of Smoluchowski's theory of diffusional collisions and Einstein's theory of diffusion, together with the simplifying assumptions that the reacting species are spherical and equal in size, with encounter radii equal to their diffusional radii. ***R*** and η are the gas constant and the viscosity of the medium respectively. Hence, $k_q\leqq(8\boldsymbol{R}T/3\eta)\times10^{-3}$. If $T=313$ and $\eta=6.56\times10^{-3}$ poise, this gives $k_q\leqq1.06\times10^{10}$ sec^{-1}, so that $\tau=1/k_s\geqq4.2\times10^{-5}$ sec., which is of a reasonable order of magnitude for a triplet of the dye in aqueous solutions at ordinary temperatures. If $1/k_s=4.2\times10^{-5}$ sec., then k_d+k_r is determined. For example, it is 9.6×10^8 l./mol. for p-Cl-$\phi\cdot$G.

Summary

The photobleaching of methylene blue in the presence of various derivatives of *N*-phenylglycine has been examined to investigate the relation between the structure and the reactivity of the electron donor and to get information about the nature of the photoreaction. The time course of the photobleaching is well expressed by the superposition of two terms decreasing exponentially with time.

The hydrogen atom on the nitrogen or α-carbon atom of the *N*-phenylglycine molecule seems to take no part in the photoreduction process, and the first stage is probably the electron transfer between the interacting species.

As judged from the initial quantum yield, Φ, of the photoreductions, the influence of substituents in the ortho- and para-positions of the benzene ring is much larger than that in the meta-position. Both electropositive and electronegative substituents reduce Φ. The small Φ in the former cases is attributed to the ability of such $\phi\cdot$G's to deactivate the excited dye ions. From spectral data, no sign of complex formation between $\phi\cdot$G's and unexcited dye molecules can be inferred. The fluorescence of methylene blue is not quenched by $\phi\cdot$G's in the range of concentrations used in the photochemical reaction. In view of these results, the kinetic data are treated by use of a current kinetic scheme, when a relation akin to Hammett's rule is found between a certain rate constant and the σ value of the substituent in the benzene ring of the *N*-phenylglycine.

Kinetic data are also used to estimate the life-time of the metastable excited state of the dye, which is calculated to be about 4.2×10^{-5} sec. or longer. This value is in a range reasonable to be interpreted as that of the lowest triplet state of the dye.

The author is indebted to Professor Ikuzo Tanaka of the Tokyo Institute of Technology

---

[13] M. Kotake, "Dai-yūkikagaku", Asakura Book Co., Tokyo (1958), p. 310.

and to Professor Masao Koizumi of Tohoku University for their constant encouragement and many helpful discussions.

Faculty of Agriculture
Kagawa University
Kita-gun, Kagawa-ken