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A MECHANISTIC STUDY OF THE PHOTOREACTION OF DIMETHYLANILINE AND METHYL CHLOROACETATE

ROLE OF ACID–BASE PROPERTIES IN BOTH THE GROUND STATE AND THE EXCITED STATE

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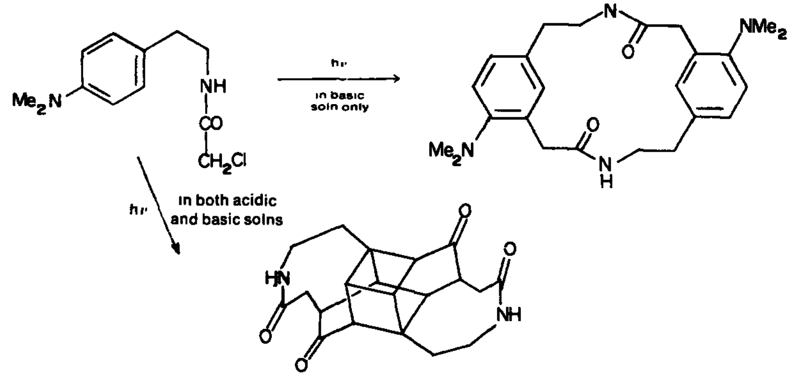
Abstract—On irradiation, dimethylaniline **1** reacted with methyl chloroacetate **2** in both acidic and basic solutions to yield methyl *o*- and *p*-dimethylaminophenylacetates (**3a**, **3b**). Kinetic treatments on the basis of quantum yields for fluorescence quenching and disappearance of **1** revealed the mechanism, which involves the exciplex in a broad sense under acidic conditions and both the exciplex and the charge-transfer complex under basic conditions.

Although the physicochemical acid–base properties of excited molecules are well documented by many researchers[1] since the initial studies by Förster[2] and Weller,[3] few photochemical reactions reflecting pK_a values of excited states and none of their kinetical treatments are known.[4] Recently, we reported the pH dependent photochemical reactions of *N*-chloroacetyl derivatives of 3- and 4-dimethylaminophenethylamines, and suggested the participation of the pK_a in the excited singlet state of the dimethylaniline chromophore.[5]



In order to clarify the mechanism of these photoreactions the intermolecular photoreaction between dimethylaniline **1** and methyl chloroacetate **2** has now been examined kinetically on the basis of quantum efficiencies of both fluorescence quenching and reaction yield.

EXPERIMENTAL

Methyl 2-dimethylaminophenylacetate **3a**. A MeOH (70 ml) soln of methyl 2-nitrophenylacetate (4.15 g) and 37% HCHO aq in the presence of 10% Pd–C (2.1 g) was hydrogenated (72 lb). After 45 min, the mixture was filtered, and the filtrate was evaporated to leave an oil, which was dissolved in ether. The ether layer was washed with 10% $NaHCO_3$, dried over Na_2SO_4, and evaporated to leave a pale yellow oil (3.52 g), b.p. 90°/0.5 Torr; ν_{max} (neat) 1735 cm^{-1}; λ_{max} (EtOH) (ϵ_{max}) 248 nm (5000); δ ($CDCl_3$) 2.58 (6H, s), 3.60 (3H, s), 3.70 (2H, s), 6.85–7.25 (4H, m); *m/e* (%) 193 (M^+, 86), 162 (27), 146 (23), 138 (100), 118 (52). Picrate, m.p. 152–153° (MeOH). (Found: C, 48.13; H, 4.27; N, 13.10. $C_{17}H_{18}N_4O_9$ requires: C, 48.34; H, 4.30; N, 13.27%).

Photoreaction of dimethylaniline **1** *and methyl chloroacetate* **2**. A 50% aqueous MeCN soln (500 ml) of dimethylaniline (**1**, 0.6 g) and methyl chloroacetate (**2**, 5.4 g) in the presence of $NaHCO_3$ (4.2 g) was irradiated under N_2 with a 100 W high pressure mercury lamp (Eikosha, Osaka) for 4 h. The reaction mixture was extracted with CH_2Cl_2, and the extract was washed with sat. NaCl aq, dried over Na_2SO_4, and evaporated to leave a pale brown oil (404 mg), which was applied to silica gel preparative TLC developing with benzene–$CHCl_3$ (4:1) to give two fractions. The upper fraction was 110 mg of **3a**, and the lower fraction was 70 mg of methyl 4-dimethylaminophenylacetate **3b** as a pale yellow oil,[6] b.p. 130°/0.5 Torr; ν_{max} (neat) 1735 cm^{-1}; λ_{max} (EtOH) (ϵ_{max}) 258 nm (16,000); δ ($CDCl_3$) 2.92 (6H, s), 3.53 (2H, s), 3.68 (3H, s), 6.69 (2H, d, J = 9 Hz), 7.17 (2H, d, J = 9 Hz); *m/e* (%) 193 (M^+, 28), 134 (100), 118 (10). (Found: C, 68.26; H, 7.92; N, 7.12. $C_{11}H_{15}NO_2$ requires: C, 68.37; H, 7.82; N, 7.25%).

Quantum yield measurements in various pH solutions. Five ml portions of 50% aqueous MeCN solns of 1 (10 mM) and 2 (50 mM) at various pH (1.0–8.8) in 15 mmϕ × 15 cm quartz test tubes were irradiated with the 2537 Å light from a 60 W low pressure mercury lamp (Eikosha OIL-60) on a merry-go-round apparatus (Rayonet MGR-500). A gas chromatograph (Shimazu GC-4A PFE) was used for quantitative analyses of the recovered 1 (3% SE-52, 80°, internal standard diethylaniline) and 3 [3% SE-52, 120–180° (8°/min), internal standard ethyl 3,4-dimethoxyphenylpropionate]. Quantum yields for the disappearance of 1 and the formation of 3 were determined relative to the 1,3-dimethyluracil actinometer[5b] photolyzed simultaneously, and the results are shown in Fig. 1.

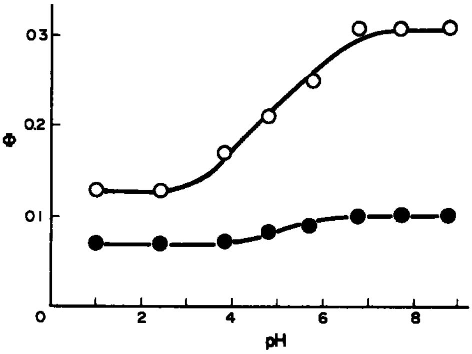


Fig. 1. Quantum yield (Φ) for the disappearance of 1 (○) and the formation of 3 (●) in the photoreaction of 1 and 2 as a function of pH.

UV Spectra of 1 *in cyclohexane in the presence of* 2. Absorption spectra of 1 (3.35×10^{-4} M) in cyclohexane in the presence of various amounts of 2 (0–5 M) were obtained on a Hitachi 323 Recording Spectrometer as shown in Fig. 2.

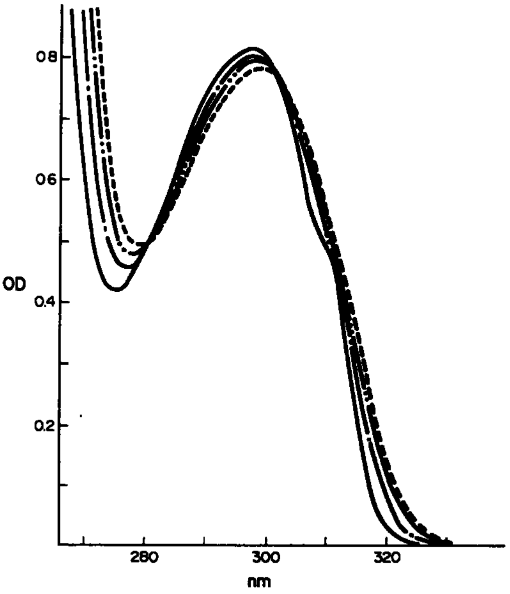


Fig. 2. Absorption spectra of 1 (3.35×10^{-4} M) in cyclohexane in the presence of various concentrations of 2: (a) none (———); (b) 1.25 M (— - —); (c) 2.5 M (— - - —); (d) 5.0 M (- - - - -).

Fluorescence quenching of 1 *with* 2. Fluorescence spectra of 50% aqueous MeCN solns of 1 (OD 0.144) with various amounts of 2 (0–100 mM) at pH 8.0 were measured using a Hitachi MPF 2A Fluorescence Spectrometer (excitation 306 nm, emission max 352 nm). The results are shown in Table 1 and plotted in Fig. 3(a). Similarly, fluorescence spectra of 1 (OD 0.22) at pH 1.65 were measured (excitation 260 nm, emission max 352 nm) as shown in Table 1 and Fig. 4.

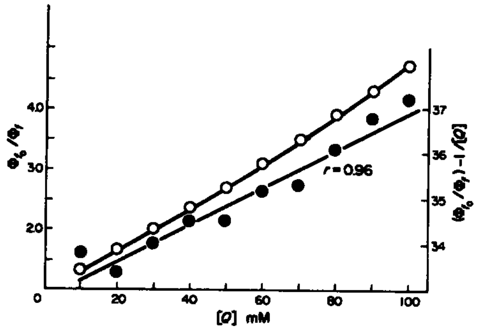


Fig. 3. Stern–Volmer plots for fluorescence quenching of 1 with 2 [Q] at pH 8.0 according to (a) eqn (2) (○) and (b) eqn (4) (●).

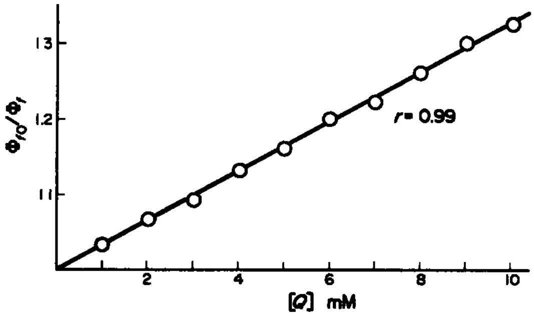


Fig. 4. Stern–Volmer plots for fluorescence quenching of 1 with 2 [Q] at pH 1.65.

Quantum yields for disappearance of 1 *in the presence of various amounts of* 2 *at pH* 7.9 *and* 1.5. Five ml portions of 50% aqueous MeCN solns of 1 (10 mM) and 2 (10–200 mM) at pH 7.9 (0.1 M phosphate buffer) and 1.5 (Walpole buffer) were irradiated with the 60 W lamp on the merry-go-round for 20 min. Quantitative analyses of 1 and quantum yield determination were performed as described above, and the results are shown in Table 2 and Fig. 5.

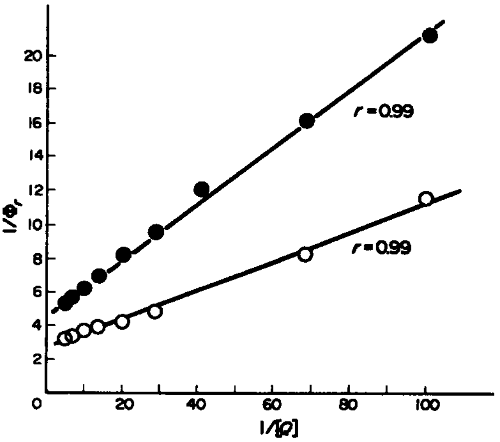


Fig. 5. Reciprocal plots of quantum yields for the disappearance of 1 at pH 7.9 (○) and 1.5 (●).

RESULTS AND DISCUSSION

A 50% aqueous MeCN solution of 1 (10 mM) and 2 (50 mM) was irradiated with a 60 W low pressure mercury lamp (practically monochromatic with the

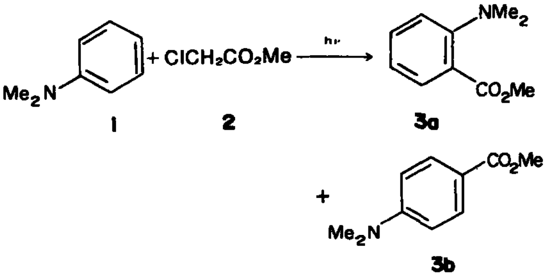
Table 1. Relative fluorescence intensities (F) and relative quantum yields (Φ_{f_0}/Φ_f) of **1** in the presence of **2** [Q] at pH 8.0 and 1.65

at pH 8.0			at pH 1.65		
[Q] (mM)	F	Φ_{f_0}/Φ_f	[Q] (mM)	F	Φ_{f_0}/Φ_f
0	100	1.00	0	100	1.000
10	74.8	1.34	1	96.6	1.035
20	60.0	1.67	2	93.9	.065
30	49.5	2.02	3	91.5	.093
40	42.0	2.38	4	88.5	1.130
50	36.7	2.72	5	86.2	1.161
60	32.1	3.12	6	83.3	1.201
70	28.8	3.47	7	81.5	1.227
80	25.7	3.89	8	79.1	1.264
90	23.2	4.31	9	77.1	1.297
100	21.2	4.72	10	75.5	1.325

Table 2. Quantum yields for disappearance of **1** in the presence of various amounts of **2** [Q] at pH 7.9 and 1.5

at pH 7.9		at pH 1.5	
[Q] (mM)	Φ_r	[Q] (mM)	Φ_r
10	0.086	10	0.047
15	0.118	15	0.062
35	0.207	25	0.083
50	0.239	35	0.105
75	0.263	50	0.121
100	0.274	75	0.146
150	0.305	100	0.163
200	0.319	150	0.179
		200	0.189

2537 Å light) in both acidic and basic solutions to give a mixture of methyl *o*- and *p*-dimethylaminophenylacetates (**3a**, **3b**).



Quantum yields for the disappearance of **1** and the formation of **3** at various pH were measured relative to the 1,3-dimethyluracil actinometer[5b] and plotted as a function of pH in Fig. 1.[7] This photoreaction proceeded even at pH lower than the ground state pK_a value (5.21)[8] of **1**. Since these types of photoreactions usually proceed via an exciplex in a broad sense between an electron-rich aromatic ring and an electron-deficient chloroacetyl group,[9] the exciplex in acidic solutions must be formed after the deprotonation of the singlet excited anilinium cation. The greater efficiency in basic solutions may be interpreted by the additive effect of a charge-transfer complex between the ground state **1** and **2**, rather than by the slow deprotonation of the anilinium cation in its excited state.[5b,10] In fact, UV spectra (Fig. 2) of **1** in cyclohexane in the presence of various amounts of **2** are quite similar to those of the charge-transfer complex between **1** and dichloromethane reported by Davis.[12] The whole scheme of principal processes in this photoreaction, therefore, can be described as follows and its validity has now been proved by the following kinetical treatment.

$$\begin{tikzcd}
(AH^+)^* \arrow[r, shift left, "k_1"] \arrow[d, shift left, "k_{f_1}\ k_{d_1}"] & A^* + Q \arrow[l, shift left, "k_{-1}"] \arrow[r, shift left, "k_q"] \arrow[d, shift left, "k_{f_2}\ k_{d_2}"] & (AQ)^* \arrow[l, shift left, "k_{-q}"] \arrow[r, shift left, "k_r"] \arrow[d, shift left, "k_{d_3}"] & \text{Product} \arrow[l, shift left] \\
AH^+ \arrow[u, shift left, "I_1"] \arrow[r, shift left, "H"] & A + Q \arrow[l, shift left, "H"] \arrow[u, shift left, "I_2"] \arrow[r, shift left] & AQ \arrow[l, shift left] \arrow[u, shift left, "k_3"] &
\end{tikzcd}$$

where A, Q, AQ and (AQ)* are **1**, **2**, the charge-transfer complex, and the exciplex, respectively. Further, k_f, k_d, k_l, k_q and k_r are the specific rate constants for fluorescence, thermal deactivation, deprotonation, exciplex formation, and reaction, respectively, and I is the rate of light absorption.

Fluorescence quenching. The fluorescence spectrum of **1** in both acidic and basic solutions has a single maximum at 352 nm, which was quenched by **2** without new emission, and this fluorescence quenching is attributable to the exciplex formation.[13] A Stern–Volmer plot in the basic solution (pH 8.0) displays slightly upward curvature (Fig. 3a), suggesting a static quenching by the charge-transfer interaction, while in the acidic solution (pH 1.65) a linear plot (correlation coefficient r = 0.99) is obtained (Fig. 4). Steady-state treatments of the scheme in acidic and basic solutions lead to respective Stern–Volmer equations (Eqns 1 and 2).

$$\frac{\Phi_{f_0}}{\Phi_f} = \frac{1+\left(1-\frac{\gamma k_{-q}}{k_r}\right)k_q\tau[Q]}{1-\left(1-\frac{k_{-q}}{k_r}\right)\left(\frac{K[Q]}{1+K[Q]}\right)} \quad \text{(in basic soln)} \tag{1}$$

$$\frac{\Phi_{f_0}}{\Phi_f} = 1+\frac{\left(1-\frac{\gamma k_{-q}}{k_r}\right)k_q\tau[Q]}{1+k_{-1}[H^+](1-a)\tau} \quad \text{(in acidic soln)} \tag{2}$$

where

$$\tau = \frac{1}{k_{d_2}+k_{f_2}}, \qquad \gamma = \frac{k_r}{k_r+k_{d_3}+k_{-q}},$$

$$K = \frac{[AQ]}{[A][Q]},$$

and

$$a = \frac{k_1}{k_1+k_{d_1}+k_{f_1}}.$$

If $\gamma k_{-q}/k_r$ and $(1-a)$ can be neglected because they are expected to be far from unity, both equations are simplified to

$$\frac{\Phi_{f_0}}{\Phi_f} = (1+K[Q])(1+k_q\tau[Q]) \quad \text{(from eqn 1)} \tag{3}$$

that is,

$$\frac{\frac{\Phi_{f_0}}{\Phi_f}-1}{[Q]} = K+k_q\tau+Kk_q\tau[Q] \tag{4}$$

and to

$$\frac{\Phi_{f_0}}{\Phi_f} = 1+k_q\tau[Q] \quad \text{(from eqn 2)} \tag{5}$$

The data in Fig. 3(a) were replotted in Fig. 3(b) according to eqn (4), and a linear plot was obtained ($r = 0.96$). The intercept $(K+k_q\tau)$ and the slope $(Kk_q\tau)$ were determined to be 32.8 and 41.2, respectively. Since the fluorescence life-time (τ) of **1** measured by the single photon counting method using a time-to-amplitude converter is 3.0 ± 0.4 nsec,[14] the dissociation constant (K) of the charge-transfer complex (AQ) and the rate constant (k_q) for the exciplex formation were calculated to be $1.31\,M^{-1}$ and $1.05\times10^{10}\,M^{-1}\,sec^{-1}$, respectively. The later value is close to the diffusion-controlled rate.[15] In the acidic solution (Fig. 4), $k_q\tau$ is 32.8, then k_q calculated from eqn (5) is $1.09\times10^{10}\,M^{-1}\,sec^{-1}$ in good agreement with the value in the basic solution.

Reaction quantum yield. The rate constant for the exciplex formation (k_q) can be also determined on the basis of reaction quantum yields. Again, steady-state treatments lead to two Stern–Volmer equations for the disappearance quantum yield (Φ_r) of **1** given by

$$\frac{1}{\Phi_r} = \frac{(1+K[Q])\left\{1+\left(1-\frac{\gamma k_{-q}}{k_r}\right)k_q\tau[Q]\right\}}{\gamma[Q](K+k_q\tau+Kk_q\tau[Q])} \text{(in basic soln)} \tag{6}$$

and

$$\frac{1}{\Phi_r} = \frac{1}{a\gamma}\left(1+\frac{1+(1-a)k_{-1}[H^+]\tau}{k_q\tau[Q]}-\frac{k_{-q}}{k_r}\right) \text{(in acidic soln).} \tag{7}$$

If $\gamma k_{-q}/k_r$, $(1-a)$ and $[Q]^2$ can be neglected, the equations are simplified to

$$\frac{1}{\Phi_r} = \frac{1}{\gamma}\left(1+\frac{1}{(K+k_q\tau)[Q]}\right) \quad \text{(from eqn 6)} \tag{8}$$

$$\frac{1}{\Phi_r} = \frac{1}{\gamma}\left(1+\frac{1}{k_q\tau[Q]}\right) \quad \text{(from eqn 7).} \tag{9}$$

The reciprocal plots of Φ_r and [Q] in basic (pH 7.9) and acidic (pH 1.5) solutions are shown in Fig. 5, and found to be linear (both $r = 0.99$). In the basic solution, the intercept ($1/\gamma$) was 2.55 and the slope $\{1/\gamma(K+k_q\tau)\}$ was 0.089, hence γ and k_q were calculated to be 0.39 and $9.2\times10^9\,M^{-1}\,sec^{-1}$, respectively, when $K = 1.31$ is substituted in eqn (8). In the acidic solution, γ is 0.22, and k_q is $9.1\times10^9\,M^{-1}\,sec^{-1}$. Both the k_q values are identical within the experimental error to those calculated from the fluorescence quenching experiments, indicating that the whole scheme indeed expresses the main processes of the photoreaction of **1** with **2**. The difference in efficiency between the two reactions in acidic and basic solutions is attributable to the difference of γ (efficiency from the exciplex to the product) and to the presence of the charge-transfer complex in the basic solution.

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[7] A mixture of photoproducts containing two and three methoxycarbonylmethyl groups was obtained over twice quantities of **3**, especially on irradiation in basic solutions. Quantum yields for the disappearance of **1** rather than those for the formation of **3**, therefore, represent the reactivity of **1**.

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[15] Since the viscosity (η) of 50% aqueous MeCN at 20° has now been measured to be 0.859 cp, the diffusion-controlled rate constant (k) if calculated from $k = 8RT/2000\eta$ is $1.14\times10^{10}\,M^{-1}\,sec^{-1}$.[16]

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