

## THE DISSOCIATION RATE OF $^1\text{O}_2(^1\Delta_g)$ DIMOL IN SOLUTION PHASE

PI-TAI CHOU\* AND YOUN-CHAN CHEN

Department of Chemistry, The National Chung-Cheng University, Chia-Yi, Taiwan, R.O.C.

(Received 28 June 1999; accepted 30 July 1999)

**Abstract**—The ratio of dissociation rate  $k_{ac}$  versus the radiative decay rate  $k_D$  of the  $^1\text{O}_2(^1\Delta_g)$  dimol has been determined to be  $1.5 \times 10^9$  by its relaxation dynamics in combination with a two-step  $\text{O}_2(^1\Delta_g)$  sensitizing tetra-*tert*-butylphthalocyanine luminescence. Consequently, with a known  $k_D$  value of  $1.2 \times 10^3 \text{ s}^{-1}$ ,<sup>10</sup>  $k_{ac}$  has been extracted to be  $1.8 \times 10^{12} \text{ s}^{-1}$  in  $\text{CDCl}_3$ .

### INTRODUCTION

Recently, attempts to obtain photophysical properties such as quantum yield, radiative lifetime, *etc.* of the  $^1\text{O}_2(^1\Delta_g)$  dimol (simplified as  $(^1\Delta_g)_2$ ) in solution phase become feasible through the direct, seminal spectroscopic detection of  $(^1\Delta_g)_2 \rightarrow (^3\Sigma^-_g)_2$  634 and 703 nm vibronic peaks.<sup>1-3</sup> Using the dimol  $(^1\Delta_g)_2 \rightarrow (^3\Sigma^-_g)_2$  emission intensity versus the tetra-*tert*-butylphthalocyanine (PC) delayed fluorescence induced by a two-step energy transfer from the  $^1\text{O}_2(^1\Delta_g)$  state,<sup>4-5</sup> we have determined the ratio between radiative decay,  $k_D$ , and dissociation rate,  $k_{ac}$ , of the  $^1\Delta_g$  dimol in  $\text{CCl}_4$ .<sup>6</sup> However, since  $k_D$  cannot be solved independently in  $\text{CCl}_4$  we simply take a  $k_D$  value of  $10 \text{ s}^{-1}$  obtained in a 4K argon matrix isolated system<sup>7</sup> and extract a lower-limit  $k_{ac}$  value of  $5.2 \times 10^{10} \text{ s}^{-1}$  in  $\text{CCl}_4$ .<sup>7</sup> We realized however that significant uncertainty might be introduced because the  $k_D$  value measured in  $\text{CCl}_4$  is expected to be different from that in the argon matrix due to different intermolecular perturbations. Very recently, we have applied Nile Blue A (NBA) as an energy acceptor and provided the first evidence<sup>8</sup> of the one-step dimol energy-transfer mechanism proposed by Khan and Kasha three decades ago.<sup>9</sup> Based on this mechanism, we have then performed a series of measurement to study the ratio of the dimol emission intensity versus that of the delayed NBA fluores-

cence as a function of the NBA concentration. As a result, a  $k_D$  value of  $1.2 \times 10^3 \text{ s}^{-1}$  in  $\text{CDCl}_3$  was deduced,<sup>10</sup> which is ~ two orders of the magnitude larger than that deduced from an argon matrix. This result implies that in addition to the geometry perturbation, the dimol may be susceptible to certain polarization perturbation which is apparently stronger than that in an argon matrix, resulting in a significant enhancement of the electric-dipole transition. In this study we have made a further attempt to resolve the dimol dissociation rate,  $k_{ac}$ , via determining the ratio of  $k_{ac}$  versus  $k_D$  in  $\text{CDCl}_3$  based on a two-step energy transfer mechanism.<sup>4-6</sup> The result leads to a reasonable estimation for the  $^1\text{O}_2$  dimol dissociation rate in  $\text{CDCl}_3$ .

### MATERIALS AND METHODS

**Materials** PC was synthesized according to the previously reported method.<sup>11</sup> The final product was purified by column chromatography (eluent:  $\text{CHCl}_3$ ). 1-H-phenalen-1-one (PH, Aldrich) was purified by column chromatography (*n*-hexane: ethyl acetate 1:1 v/v) followed by twice recrystallization from methanol.  $\text{C}_{60}$  was purified by chromatography on neutral alumina according to the previous report.<sup>12</sup>  $\text{CDCl}_3$  (99.8 %, Merck) free from trimethoxysilane, a standard reagent for the proton NMR which quenches  $^1\text{O}_2$  significantly, was used right after received. For the  $\text{O}_2(^1\Delta_g)$  sensitizing PC experiment,  $\text{C}_{60}$  was used as a photosensitizer to generate  $\text{O}_2(^1\Delta_g)$ . Normally, an optical density of 0.5 was prepared at 514 nm, corresponding to a concentration of  $\text{C}_{60}$  of  $5.5 \times 10^{-4} \text{ M}$  ( $\epsilon_{514} = 960 \text{ l mol}^{-1}\text{cm}^{-1}$  in  $\text{CHCl}_3$ ). PC was prepared in the absorbance range of 0.1-1.67 at 700 nm, corresponding to a concentration in the range of  $6.0 \times 10^{-7}$  to  $1.0 \times 10^{-5} \text{ M}$  ( $\epsilon_{700} = 1.67 \times 10^5 \text{ l mol}^{-1}\text{cm}^{-1}$  in  $\text{CDCl}_3$ ). Under such concentrations, the optical density of PC is between  $5 \times 10^{-4}$  and  $7.5 \times 10^{-3}$  at 514 nm. Therefore, the PC prompt fluorescence interference resulting from the direct 514 nm excitation is small and can be completely eliminated from the sensitized PC fluorescence at a delay time of 10  $\mu\text{s}$  (see the next section for details). The sample cuvette was excited at the edge of the fluorescence cell to avoid the inner filter effect.

**Method** The spectral detection in the region of 600-800 nm

\* To whom the correspondence should be addressed.

<sup>†</sup> In reference 6 a factor of 2 in the denominator of eq. (1) has to be deleted. Accordingly, the estimated  $k_{ac}$  value of  $2.6 \times 10^{10} \text{ s}^{-1}$  in  $\text{CCl}_4$  is changed to  $5.2 \times 10^{10} \text{ s}^{-1}$ .

<sup>‡</sup> In this study the lifetime of the  $^1\text{O}_2$  dimol, depending on the laser power, is in the range of 1.0 to 2.5 ms. Therefore, a gate window of 20 ms should sufficiently acquire > 99 % of the emission intensity.

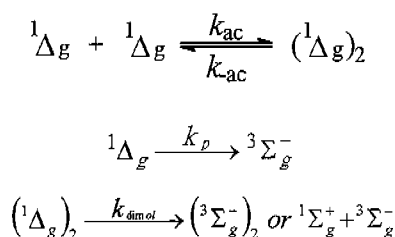
<sup>§</sup> In a typical experiment when a concentration of  $\text{C}_{60}$  was prepared so that the absorbance is 0.5 at 514 nm, an upper-limit value of  $1.0 \times 10^{-6} \text{ M}$  for  $^1\text{O}_2$  production was estimated upon 514 nm (50 mW, 300  $\mu\text{s}$  duration time) excitation.

was accomplished by a red-sensitive intensified charge coupled detector (ICCD, Princeton Instrument, Model 576G/1) coupled with a polychromator in which the grating is blazed with a maximum at 700 nm. Variable time delay and window duration selected to gate the ICCD was achieved by a high-voltage pulse amplifier (Princeton Instrument, PG 200). In this study, an Ar<sup>+</sup> laser (coherent Innova 5W, 362 or 514 nm) was modulated by a mechanic chopper (Standard Research System, model 540) in which the space between two blazes has been modified to achieve a 3 Hz, 200  $\mu$ s square pulse output. Therefore, the luminescence can be acquired at variable delay times to eliminate the prompt fluorescence of the sensitizers upon direct excitation. The low power Ar<sup>+</sup> laser significantly reduces the power-dependent photochemical production of <sup>1</sup>O<sub>2</sub> quenchers in the halogenated solvents.<sup>13-17</sup> As a result, the lifetime of the O<sub>2</sub>(<sup>1</sup> $\Delta_g$ ) species increases, enhancing the dimol emission intensity. In this study, the gate of the ICCD was open at a delay time of 10  $\mu$ s and a window duration was typically set as wide as 20 ms to eliminate the prompt fluorescence but still cover the entire decay region (> 99 %) of the delayed luminescence in CDCl<sub>3</sub>.<sup>#</sup> For steady-state measurements in the region of 1000-1700 nm, we applied a Fourier transform technique in which the sample was excited by an Ar ion laser (Coherent Innova 90) pumped dye laser (Coherent 599-01A) under a front-face excitation configuration. The emission was sent through a near-IR interferometer (Bruker Equinox 55) and detected by a liquid nitrogen cooled Ge detector (403X, Applied Detector Corporation). For the time-resolved measurement of the O<sub>2</sub>(<sup>1</sup> $\Delta_g$ ) emission a liquid nitrogen cooled Ge photodiode (Applied Detector Corporation model 403HS) was used. The output signal was amplified by a linear amplifier (Stanford Research System, model 445) and then sent through a 2.5 GHz bandwidth transient digitizer (Leeroy 9361) for the lifetime analysis.

## RESULTS AND DISCUSSION

Scheme 1 depicts the generation and relaxation of the <sup>1</sup>O<sub>2</sub> dimol, [(<sup>1</sup> $\Delta_g$ )<sub>2</sub>], in a typical dye sensitization mechanism where the rise kinetics of the O<sub>2</sub>(<sup>1</sup> $\Delta_g$ ) state is neglected due to the much faster formation rate than the decay of O<sub>2</sub>(<sup>1</sup> $\Delta_g$ ) in CDCl<sub>3</sub>.

Applying a steady-state approximation, the time-dependent



Scheme 1.

<sup>1</sup>O<sub>2</sub> dimol concentration, [(<sup>1</sup> $\Delta_g$ )<sub>2</sub>], concentration can be expressed as [(<sup>1</sup> $\Delta_g$ )<sub>2</sub>] =  $\frac{k_{ac}}{k_{ac} + k_{ac}'} [^1\Delta_g]_0 e^{-2k_p t}$ .<sup>10</sup> Accordingly, the integrated O<sub>2</sub>(<sup>1</sup> $\Delta_g$ ) dimol emission intensity, I<sub>dim</sub>, can be expressed as

$$I_{dim} = \frac{\alpha k_D k_{ac}}{2k_p k_{-ac}} [^1\Delta_g]_0^2 \quad (1-1)$$

where  $\alpha$  is the instrument factor, including sensitivity, alignment, etc. of the detecting system.  $k_D$  is the O<sub>2</sub>(<sup>1</sup> $\Delta_g$ ) dimol radiative decay rate, which may be distinguished from  $k_{dimol}$  shown in Scheme I by knowing  $k_{dimol} = k_D + k_{nr}$  where  $k_{nr}$  is the sum of overall nonradiative decay processes except for  $k_{-ac}$ .

Fig. 1 shows the (<sup>1</sup> $\Delta_g$ )<sub>2</sub> → (<sup>3</sup> $\Sigma_g^-$ )<sub>2</sub> dimol transition as well as the time-dependent O<sub>2</sub>(<sup>1</sup> $\Delta_g$ ) sensitizing PC delayed fluorescence in CDCl<sub>3</sub>. The decay rate of the PC delayed fluo-

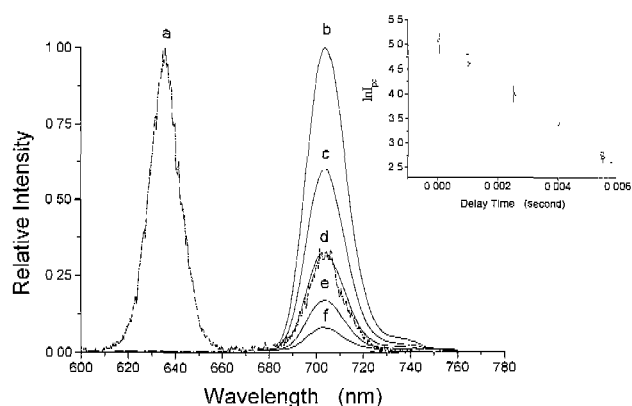
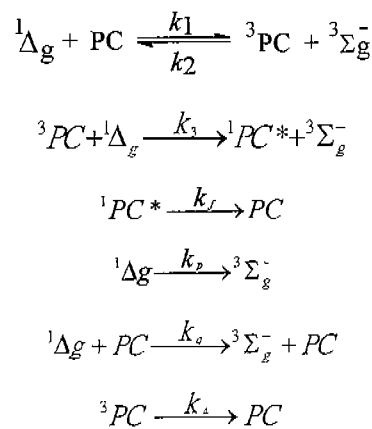


Figure 1. **a.** (—) The spectrum of the C<sub>60</sub> ( $5.5 \times 10^{-4}$  M) sensitized O<sub>2</sub>(<sup>1</sup> $\Delta_g$ ) dimol emission obtained at a delay time of 10  $\mu$ s with a gate window open as large as 20 ms. **b-f.** (—) Similar conditions as **a.** except that the PC concentration of  $6.0 \times 10^{-7}$  M was added. The spectra were obtained at a delay time of **b.** 50  $\mu$ s, **c.** 1.0 ms, **d.** 2.5 ms, **e.** 4.0 ms, **f.** 5.5 ms and with a gate width of 200  $\mu$ s. In this study, a chopped 514 nm Ar<sup>+</sup> laser line (200  $\mu$ s pulse, 40 mW) was used as an excitation source. The solution was air aerated at 1.0 atm, 298 K. Note that spectrum **a.** has been normalized to the same intensity as spectrum **b.** Insert: the logarithm of the integrated PC emission intensity as a function of the delay time.

rescence has been reported to be twice as fast as the decay rate of O<sub>2</sub>(<sup>1</sup> $\Delta_g$ ), and its relaxation dynamics can be well explained by a two-step energy-transfer mechanism<sup>4,6</sup> depicted as follows



Scheme 2.

Accordingly, the time-dependent [ $^1\Delta_g$ ], [ $^3\text{PC}$ ] and [ $^1\text{PC}^*$ ] can be expressed in sequence by (2-1), (2-2) and (2-3), respectively.

$$\frac{d[{}^1\Delta_g]}{dt} = -k_1[\text{PC}][{}^1\Delta_g] + k_2[{}^3\Sigma_g^-][{}^3\text{PC}] - k_3[{}^3\text{PC}][{}^1\Delta_g] - (k_p + k_q[\text{PC}])[{}^1\Delta_g] \quad (2-1)$$

$$\frac{d[{}^3\text{PC}]}{dt} = k_1[{}^1\Delta_g][\text{PC}] - k_2[{}^3\Sigma_g^-][{}^3\text{PC}] - k_3[{}^1\Delta_g][{}^3\text{PC}] - k_4[{}^3\text{PC}] \quad (2-2)$$

$$\frac{d[{}^1\text{PC}^*]}{dt} = k_3[{}^3\text{PC}][{}^1\Delta_g] - k_f[{}^1\text{PC}^*] \quad (2-3)$$

For the case of PC,  $k_1/k_2$  has been estimated to be  $\sim 2.0 \times 10^{-3}$  based on the energy difference between  $^3\text{PC}$  and  $\text{O}_2$  ( $^1\Delta_g$ ) states (*vide infra*). In addition,  $\text{O}_2[{}^3\Sigma_g^-]$  was prepared to be  $2.05 \times 10^{-3}$  M in the aerated solution,<sup>18</sup> which is  $\gg \text{O}_2[{}^1\Delta_g]$  produced ( $< 1.0 \times 10^{-6}$  M<sup>6</sup>) in this study. As a result,  $k_2[{}^3\Sigma_g^-]$  is  $\gg k_1[{}^1\Delta_g]$  during the reaction, and a steady-state approach can be applied for [ $^3\text{PC}$ ] shown in (2-2) to obtain

$$k_1[\text{PC}][{}^1\Delta_g] - (k_2[{}^3\Sigma_g^-] + k_3[{}^1\Delta_g] + k_4)[{}^3\text{PC}] = 0$$

$$\therefore [{}^3\text{PC}] = \frac{k_1[\text{PC}][{}^1\Delta_g]}{k_2[{}^3\Sigma_g^-] + k_3[{}^1\Delta_g] + k_4} \quad (2-4)$$

We have also performed a triplet-triplet transient absorption study of PC under a degassed condition and determined  $k_4$  to be  $\sim 6.2 \times 10^4$  s<sup>-1</sup> in room temperature  $\text{CDCl}_3$ . On the other hand, due to the highly exothermic  $^3\text{PC} + {}^3\Sigma_g^- \xrightarrow{k_3} \text{PC} + {}^1\Delta_g$ <sup>1,6,19,20</sup> and  $^3\text{PC} + {}^1\Delta_g \xrightarrow{k_3} {}^1\text{PC}^* + {}^3\Sigma_g^-$  processes, it is reasonable to assume  $k_3$  to be a diffusion controlled rate which is  $1.34 \times 10^{10}$  M<sup>-1</sup>s<sup>-1</sup> calculated from the Debye equation.  $k_2$  can be treated as a typical sensitization rate constant to produce ( $^1\Delta_g$ ) which is theoretically taken to be 1/9 of the diffusion controlled rate, *i.e.*  $1.5 \times 10^9$  s<sup>-1</sup> in  $\text{CDCl}_3$ . Due to the small  $^1\text{O}_2$  production, it is apparent that  $k_2[{}^3\Sigma_g^-]$  is much greater than  $k_3[{}^1\Delta_g] + k_4$ . Consequently, (2-4) can be further simplified to

$$[{}^3\text{PC}] \approx \frac{k_1[\text{PC}][{}^1\Delta_g]}{k_2[{}^3\Sigma_g^-]} \quad (2-5)$$

Plugging (2-5) to (2-1) we obtain

$$\frac{d[{}^1\Delta_g]}{dt} = -\frac{k_1 k_3 [\text{PC}][{}^1\Delta_g]^2}{k_2 [{}^3\Sigma_g^-]} - (k_p + k_q [\text{PC}])[{}^1\Delta_g] \quad (2-6)$$

(2-6) can be solved by applying the Bernoulli equation to obtain

$$[{}^1\Delta_g] = \frac{(k_p + k_q [\text{PC}])[{}^1\Delta_g]_0}{\left( (k_p + k_q [\text{PC}]) + \frac{k_1 k_3 [\text{PC}]}{k_2 [{}^3\Sigma_g^-]} [{}^1\Delta_g]_0 \right) e^{k_f t} - \frac{k_1 k_3 [\text{PC}]}{k_2 [{}^3\Sigma_g^-]} [{}^1\Delta_g]_0} \quad (2-7)$$

Since [PC] was prepared in the range of  $6.0 \times 10^{-7}$  to  $1.0 \times 10^{-5}$  M, an upper limit of  $\frac{k_1 k_3 [\text{PC}][{}^1\Delta_g]_0}{k_2 [{}^3\Sigma_g^-]}$  was estimated to

be  $2.1 \times 10^{-2}$  which is much smaller than  $(k_p + k_q[\text{PC}])$  measured in  $\text{CDCl}_3$ .<sup>10</sup> Therefore,  $(k_p + k_q[\text{PC}])$  is  $\gg$

$\frac{k_1 k_3 [\text{PC}][{}^1\Delta_g]_0}{k_2 [{}^3\Sigma_g^-]}$ , and (2-7) can be further simplified to

$$[{}^1\Delta_g] \approx [{}^1\Delta_g]_0 e^{-(k_p + k_q [\text{PC}])t}, \text{ and } [{}^3\text{PC}] \approx \frac{k_1 [\text{PC}][{}^1\Delta_g]_0 e^{-(k_p + k_q [\text{PC}])t}}{k_2 [{}^3\Sigma_g^-]} \quad (2-8)$$

Plugging (2-8) to (2-3) and using an ordinary, homogeneous first order differential equation to solve [ $^1\text{PC}^*$ ], we obtain

$$[{}^1\text{PC}^*] = \frac{k_1 k_3 [\text{PC}][{}^1\Delta_g]_0^2}{k_2 [{}^3\Sigma_g^-] (k_f - 2(k_p + k_q [\text{PC}]))} \left[ e^{-2(k_p + k_q [\text{PC}])t} - e^{-k_f t} \right] \quad (2-9)$$

Since  $k_f$  is  $\gg (k_p + k_q[\text{PC}])$ , (2-9) can be simplified to (2-10) at the decay time of interest (*e.g.*  $> 10$   $\mu\text{s}$ ).

$$[{}^1\text{PC}^*] \approx \frac{k_1 k_3 [\text{PC}][{}^1\Delta_g]_0^2}{k_2 k_f [{}^3\Sigma_g^-]} e^{-2(k_p + k_q [\text{PC}])t} \quad (2-10)$$

Consequently, the integrated emission intensity of [ $^1\text{PC}^*$ ] can be expressed as

$$F_{\infty} = \alpha \times \frac{k_f^{\text{PC}} k_1 k_3 [\text{PC}][{}^1\Delta_g]_0^2}{2(k_p + k_q [\text{PC}]) k_f^{\text{PC}} k_2 [{}^3\Sigma_g^-]} \quad \text{where } k_f^{\text{PC}} \text{ is the radiative}$$

decay rate of  $^1\text{PC}^*$ .

Under an identical experimental configuration, *i.e.* the same  $\alpha$  value and number of photons being absorbed, the ratio of the sensitized PC fluorescence intensity versus the dimol emission intensity can be expressed as

$$F_{\text{PC}} = \alpha \times \frac{k_f^{\text{PC}} k_1 k_3 [\text{PC}][{}^1\Delta_g]_0^2}{2(k_p + k_q [\text{PC}]) k_f^{\text{PC}} k_2 [{}^3\Sigma_g^-]} \quad (2-11)$$

The value of  $\frac{k_f^{\text{PC}}}{k_f^{\text{PC}}}$  is equivalent to the fluorescence yield of PC, which was determined in this study to be 0.75 in  $\text{CDCl}_3$ .  $k_1/k_2$  is simply the equilibrium constant between ( $^1\Delta_g$ ) and PC ( $T_1$ ), which has been determined to be  $1.5 \times 10^{-3}$  based on the  $T_1$ - $S_0$  phosphorescence energy gap measured in the 77K methyltetrahydrofuran (MTHF) glass.<sup>6</sup> Since the fluorescence maximum of PC only reveals slight solvent-polarity dependence, which is red shifted from 702 nm in MTHF to 705 nm in  $\text{CDCl}_3$ , it is reasonable to predict a similar bathochromic shift in the triplet state.<sup>19,20</sup> Accordingly, a  $T_1$ - $S_0$  energy gap of 9120 cm<sup>-1</sup> was estimated in  $\text{CDCl}_3$ , giving rise to a  $k_1/k_2$  value of  $2.0 \times 10^{-3}$ . Furthermore, it is reasonable to assume that both  $k_3$  (*vide supra*) and  $k_{ic}$  are diffusion controlled processes and can be canceled out. Giving the  $\text{O}_2({}^3\Sigma_g^-)$  concentration to be  $2.05 \times 10^{-3}$  M in the aerated  $\text{CDCl}_3$ , (2-11) can be simplified to

$$\frac{F_{\text{PC}}}{I_{\text{dimol}}} = 0.73 \left( \frac{k_{\text{ae}}}{k_D} \right) \left( \frac{k_p}{k_p + k_q [\text{PC}]} \right) [\text{PC}] \quad (2-12)$$

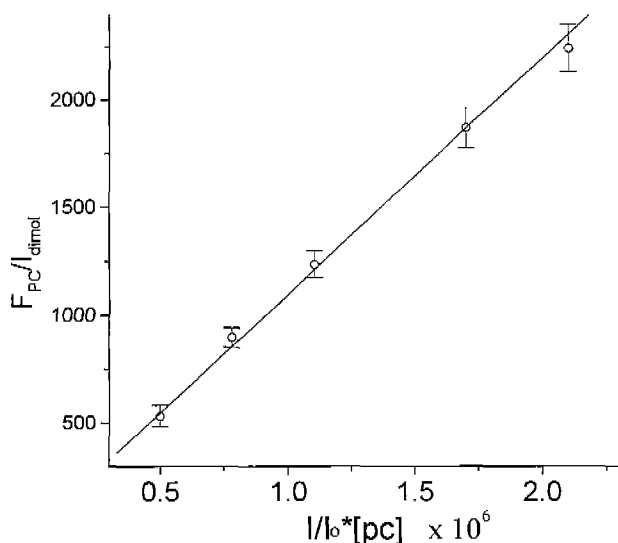


Figure 2. The plot of  $\frac{F_{PC}}{I_{dimol}}$  versus  $\frac{I}{I_0} [PC]$  from [PC] of a.  $6.0 \times 10^{-7}$ , b.  $1.2 \times 10^{-6}$ , c.  $2.0 \times 10^{-6}$ , d.  $5.0 \times 10^{-6}$  and e.  $1.0 \times 10^{-5}$  M, and its best least-square fitted line (see the text for the detailed description).

The quenching rate constant  $k_q$  of PC to  $O_2(^1A_g)$  has been determined to be  $2.6 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$  in  $\text{CHCl}_3$ .<sup>6, 20</sup> Therefore, it seems relatively straightforward to obtain the value of  $k_p/(k_p + k_q[PC])$  once [PC] and  $k_p$  are known. However, since  $k_p$  in  $\text{CDCl}_3$  is dependent on the laser intensity,<sup>8</sup> this procedure seems to be complicated in a power-dependent study. Alternatively we simply applied a Stern-Volmer relationship using  $(^1A_g) \rightarrow ^3\Sigma_g^-(0,0)$  1273 nm emission intensity shown in eq. (2-12) to replace  $k_p/(k_p + k_q[PC])$

$$\frac{F_{PC}}{I_{dimol}} = 0.73 \left( \frac{k_{-ac}}{k_D} \right) \left( \frac{I}{I_0} \right) [PC] \quad (2-13)$$

where  $I_0$  and  $I$  denote the PH sensitizing  $(^1A_g)$  1273 nm emission in  $\text{CDCl}_3$  and  $\text{CDCl}_3$  containing PC, respectively. Experimentally, the  $F_{PC}/I_{dimol}$  value, within the experimental error, was found to be linearly proportional to  $\left[ \frac{I}{I_0} \right] \times [PC]$  when the PC concentration varied from  $6.0 \times 10^{-7}$  to  $1.0 \times 10^{-5}$  M (see Fig. 2), consistent with the theoretical approach depicted in eq. (2-13). The slope in Fig. 2 was determined to be  $1.1 \times 10^9 \text{ M}^{-1}$ . This gives a  $k_{ac}/k_D$  value of  $1.5 \times 10^9$ . Since  $k_D$  in  $\text{CDCl}_3$  has been determined to be  $1.2 \times 10^3 \text{ s}^{-1}$ ,<sup>10</sup> a  $k_{ac}$  value of  $1.8 \times 10^{12} \text{ s}^{-1}$  was then deduced. This calculated  $\tau_{ac}$  ( $= 1/k_{ac}$ ) of  $\sim 550$  fs is about one order of magnitude faster than the estimated dissociation rate in the gas phase of few picoseconds.<sup>21</sup> On another approach, based on the dissociation of the dimol yielding singlet sigma oxygen, the dimol dissociation rate of  $3.5 \times 10^{11} \text{ s}^{-1}$  has been estimated in  $\text{CCl}_4$ ,<sup>22</sup> indicating a possibility that the solvent polarization may play a role in assisting the dissociation of the dimol species. The generalization of  $k_{ac}$  value as a function of the solvent properties requires further works on the solvent-dependence for both  $k_p$  and  $k_{ac}$  values. Unfortunately, the study of solvent-dependent  $k_p$  is not feasible at this stage due to the sparse

solubility of NBA in many halogenated and/or deuterated solvents where the dimol emission is detectable due to the long life span of the  $^1O_2$  emission. Focus on the synthesis of NBA derivatives in order to improve its solubility is currently in progress.

*Acknowledgment*—Support from the National Chung-Cheng University and National Science Council (grant NSC85-2113-M-194-005) is gratefully acknowledged.

## REFERENCES

1. Krasnovsky, Jr., A. A. and K. V. Neverof (1990) Photoinduced dimol luminescence of singlet molecular oxygen in solutions of photosensitizers. *Chem. Phys. Lett.* **167**, 591-596.
2. Chou, P. T., G. T. Wei, C. H. Lin, C. Y. Wei and C. H. Chang (1996) Direct spectroscopic evidence of photosensitized  $O_2$  765 nm ( $^1\Sigma_g^+ \rightarrow ^3\Sigma_g^-$ ) and  $O_2$  dimol 634 and 703 nm ( $(^1A_g)_2 \rightarrow (^3\Sigma_g^-)_2$ ) vibronic emission in solution. *J. Am. Chem. Soc.* **118**, 3031-3032.
3. Chou, P. T., Y. C. Chen, C. Y. Wei, S. J. Chen, H. L. Lu and M. Z. Lee (1997) The sensitized  $O_2$  ( $^1A_g$ ) dimol luminescence in solution. *Chem. Phys. Lett.* **280**, 134-140.
4. Krasnovsky Jr., A. A. and C. S. Foote (1993) Time-resolved measurements of singlet oxygen dimol-sensitized luminescence. *J. Am. Chem. Soc.* **115**, 6013-6016.
5. Gorman, A. A., I. Hamblett and T. J. Hill (1995) Evidence against "dimol-sensitized luminescence" in solutions containing singlet oxygen. *J. Am. Chem. Soc.* **117**, 10751-10752.
6. Chou, P. T., Y. C. Chen, C. Y. Wei, S. J. Chen, H. L. Lu and T. H. Wei (1997) Photophysical properties of  $(O_2(^1A_g))_2$  and  $O_2(^1A_g^+)$  in solution phase. *J. Phys. Chem.* **101A**, 8581-8586.
7. Becher, A. C., U. Schurath, H. Dubost and J. P. Galaup (1988) Luminescence of metastable  $^{16}O_2$  ( $^1O_2$ ) in solid argon; relaxation and energy transfer. *Chem. Phys.* **125**, 321-336.
8. Chou, P. T., Y. C. Chen, C. Y. Wei and M. Z. Lee (1998) Evidence on the  $O_2$  ( $^1A_g$ ) dimol-sensitized luminescence in solution. *J. Am. Chem. Soc.* **120**, 4883-4484.
9. Khan, A. U. and M. Kasha (1970) Chemiluminescence arising from simultaneous transition in pairs of singlet oxygen molecules. *J. Am. Chem. Soc.* **92**, 3293-3300.
10. Chou, P. T., Y. C. Chen and C. Y. Wei (1998) Photophysical properties of  $(O_2(^1A_g))_2$  in solution phase. *Chem. Phys. Lett.* **294**, 579-583.
11. Mikhalenko, S. A., O. L. Barkianova, L. O. Lebedev and E. A. Lukjanetz (1971) Phthalocyanines and related compounds IX. Synthesis and electronic absorption spectra of tetra-4-*tert*-butyl phthalocyanine. *Zh. Obshch. Khim. (J. Gen. Chem. USSR)*, **41**, 2735-2739.
12. Ajje, H. M. M. Alvarez, S. A. Anz, R. D. Beck, F. Diederich, K. Fostiropoulos, D. R. Huffman, W. Kratschmer, Y. Rubin,

- K. E. Schriver, D. Sensharma and R. L. Whetten (1990) Characterization of the soluble all-carbon molecules  $\text{C}_{60}$  and  $\text{C}_{70}$ . *J. Phys. Chem.* **94**, 8630-8633.
13. Krasnovsky, Jr. A. A. (1979) Photoluminescence of singlet oxygen in pigment solutions. *Photochem. Photobiol.* **29**, 29-36.
14. Salokhiddinov, K. I., D. M. Dzhagarov, I. M. Byteva and G. P. Guinovich (1980) Photosensitized luminescence of singlet oxygen in solutions at 1588 nm. *Chem. Phys. Letts.* **76**, 85-87.
15. Hurst, J. R. and G. B. Schuster (1983) Nonradiative relaxation of singlet oxygen in solution. *J. Am. Chem. Soc.* **105**, 5756-5760.
16. Chou, P. T. and H. Frei (1985) Sensitization of molecular oxygen  ${}^1\Sigma_g^+ \rightarrow {}^1\Delta_g$  emission in solution, and observation of molecular oxygen  ${}^1\Delta_g \rightarrow {}^3\Sigma_g^-$  chemiluminescence upon decomposition of 1,4-dimethylnaphthalene endoperoxide. *Chem. Phys. Letts.* **122**, 87-92.
17. Schmidt, R. and H. D. Brauer (1987) Radiationless deactivation of singlet oxygen ( ${}^1\Delta_g$ ) by solvent molecules. *J. Am. Chem. Soc.* **109**, 6976-6981.
18. Monroe, B. M. (1982) Photochemical estimation of oxygen solubility. *Photochem. Photobiol.* **34**(6), 863-865.
19. Vincett, P. S., E. M. Voigt and K. E. Rieckhoff (1971) Phosphorescence and fluorescence of phthalocyanines. *J. Phys. Chem.* **55**, 4131-4140.
20. Krasnovsky, Jr., A. A., M. A. J. Rogers, M. G. Galpern, B. Rither, M. E. Kenny and E. A. Lukjanetz (1992) Quenching of singlet molecular oxygen by phthalocyanines and naphthalocyanines. *Photochem. Photobiol.* **55**, 691-696.
21. Arnold, S. J., M. Kubo and E. A. Ogryzlo (1968) Relaxation and reactivity of singlet oxygen. *Adv. Chem. Ser.* **77**, 133-142.
22. Scurlock, R. D. and P. R. Ogilby (1996) Quenching of  $\text{O}_2({}^1\Delta_g)$  by  $\text{O}_2({}^1\Delta_g)$  in Solution. *J. Phys. Chem.* **100**, 17226-17231.