# REACTION OF SINGLET OXYGEN WITH 2-PYRAZOLINE: IMPLICATION FOR CATION RADICAL - SUPEROXIDE ION PAIR INTERMEDIATE

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Abstract: Kinetic studies on photosensitized oxygenation of 1,3,5triary1-2-pyrazolines show that an electron-transfer from the pyrazoline to singlet oxygen may take place to give a cation radical and superoxide ion pair. The reaction of pyrazoline cation radicals with superoxide ion shows the same product distribution with singlet oxygenation.

### Introduction

Much attention has been drawn to photosensitized oxygenation of electron-rich substrates such as olefins,<sup>1)</sup> amines,<sup>2)</sup> and sulfides,<sup>3,4)</sup> in which an electron-transfer from the substrate to singlet oxygen may take place to afford a cation radical-superoxide ion pair.<sup>5)</sup> Recombination of the ion pair would give the oxidized product and/or back-transfer of an electron would give quenching of singlet oxygen.<sup>5)</sup> Recently, we have found that the photosensitized oxygenation of 1,3,5-triaryl-2-pyrazolines led to dehydrogenation to the corresponding pyrazoles but some of them are extremely stable and capable of quenching of singlet oxygen efficiently.<sup>6,7)</sup>



These results have prompted us to clarify the reaction mechanism of photosensitized oxygenation of 2-pyrazolines. We wish to report here kinetic and chemical evidences to support the formation of a cation radical and superoxide ion pair intermediate in the pyrazoline photooxidation.<sup>4</sup>)

### Results and Discussion

## Photosensitized Oxygenation of 2-Pyrazoline: Kinetic Measurement

Photosensitized oxygenation of 2-pyrazolines gave the pyrazole 2. Control experiments show that 2-pyrazolines  $(\underline{1a}-\underline{h})$  are stable under the reaction conditions in the absence of the sensitizer or light. Addition of 1-phenyl-3-(p-diethylaminostyryl)-5-(p-diethylaminophenyl)-2-pyrazoline ( $\underline{1i}$ ) as a singlet oxygen quencher<sup>6</sup>) inhibited the oxidation of  $\underline{1a}$ . These data suggest that the present

reaction is a singlet oxygenation. The reaction rates of photosensitized oxygenation of 2-pyrazolines are listed in Table. The rates of the photooxidation decrease with the increase of electron- donating ability of substituents on both 3- and 5-phenyl group and log( $k_{rel}$ )'s are correlated with the Hammet $\sigma$ -constants( $\rho$  =+1.54 for <u>1a-d</u>;  $\rho$ =+0.47 for <u>1a,e-g</u>), but not with the Brown-Okamoto's  $\sigma^+$ -constants or oxidation potentials.<sup>6</sup>)

Scheme I holds for photosensitized oxygenation of pyrazoline <u>A</u>, where  $k_e$ ,  $k_q$ , and  $k_r$  are the rate constants of electron-transfer, quenching, and pyrazole formation, respectively. The rate of pyrazole formation is given by eq.1.  $[^1O_2]$  is the concentration of singlet oxygen generated in the reaction course. Assuming  $k_q \gg k_r$  from the results of relative rates for 2-pyrazolines <u>1</u>, the Hammet free-energy relationship and the relationship in signs between  $\rho_e$ ,  $\rho_r$ , and  $\rho_q$  are expressed as eq.2. It seems to be clear that electron-donating substituents might prompt the electron-transfer process ( $\rho_e; \Theta$ ) but suppress the reverse one ( $\rho_q; \Theta$ ).<sup>6</sup> As a result from that the observed  $\rho$  value is positive, the value of  $\rho_r$  has to be positive.<sup>8</sup> This means that the deprotonation from pyrazoline cation

a Ep vs SCE(V)<sup>b</sup> ρ(vs σ) 2-pyrazoline k<sub>rel</sub> ۵ <u>1b;</u> X=Cl 2.1 0.89 0.23 +1.54 (0.966)<sup>C</sup> 0.89 0 1.0 н <u>a;</u> 0.7 0.84 -0.17 <u>c;</u> Me d; OMe 0.3 0.79 -0.27 0.89 0.23 +0.47 <u>e;</u> Y=Cl 1.5 (0.891)<sup>C</sup> -0.17 1.1 0.86 <u>f;</u> Mo 0.85 -0.27 0.8 OMe g; \_ 0.79 h; NMe<sub>2</sub>

Table. Comparison of Kinetics with Oxidation Potential(E ), the Hammet  $\sigma$ -Constant and  $\rho$ -Value

a) Average values for at least 5 experiments.

b) Oxidation potentials listed indicate the first peak potentials of the pyrazoline.

c) Correlation ciefficient.

radical A<sup>‡</sup> takes place.

Scheme I.

$$\mathbf{A} + {}^{1}\mathbf{O}_{2} \xrightarrow{\mathbf{k}_{e}} [\mathbf{A}^{\dagger} + \mathbf{O}_{2}^{\dagger}] \xrightarrow{\mathbf{k}_{r}} \mathbf{AO}_{2}$$

$$\mathbf{k}_{q} = \mathbf{A} + {}^{3}\mathbf{O}_{2}$$

---- eg.1

Rate = 
$$[k_e k_r / (k_r + k_g)][A][_0_2]$$

$$\log(k_{obs})_{rel} = \log(k_e)_{rel} + \log(k_r)_{rel} - \log(k_q)_{rel}$$
$$= (\rho_e + \rho_r - \rho_a) \sigma = \rho_{obs} \cdot \sigma \qquad ----- eq.2$$

ρ <sub>e</sub>	°r	Pq	$(\rho_e + \rho_r - \rho_q)$	ado <sup>q</sup>
_	-	+	-	+
-	+	+	+ or -	+

Separate kinetic runs for photosensitized oxygenation of 5-deuterated <u>1a</u> and undeuterated <u>1a</u> show the  $k_H/k_D = 2.1$  supporting that the deprotonation should be the rate-determing step.<sup>9</sup>) Reactivities of 3-methoxyphenyl pyrazoline <u>1d</u> and 5dimethylaminophenyl pyrazoline <u>1h</u> were quite different (100% and less than 5% conversion, respectively, under the same condition), even though they have the same oxidation potential (Ep=+0.79 V vs. SCE). The formation of hydrogen peroxide in the reaction mixture was confirmed by means of a potassium iodide test.

One plausible rationale for these observations seems that singlet oxygenation of 2-pyrazolines proceeds via an electron-transfer process and the deprotonation on 5-position of pyrazoline cation radical might be the rate-determing step as shown in Scheme 2. To test these possibilities, we have investigated the reaction of 2pyrazoline cation radicals with superoxide ion in comparison with singlet oxygenation.



Reaction of Pyrazoline Cation Radicals with Superoxide Ion

The cation radical  $\underline{3a}$  from  $\underline{1a}$  was prepared by mixing solutions of  $\underline{1a}$  and nitrosonium tetrafluoroborate (NOBF $_4$ ) as an one-electron oxidizing agent in dry acetonitrile on a vacuum line.<sup>4)</sup> After removing the evolved NO and solvent, the residue was dissolved again in dry acetonitrile. A dark-brown colored solution with a maximum absorbance at 410 nm was obtained (Fig.). This solution gave an ESR spectrum with g value of 2.0033,<sup>10)</sup> which is attributed to an organic cation radical,<u>3a</u>. The cation radicals <u>3h</u> ( $\lambda$  max=406 nm) and <u>3i</u> ( $\lambda$  max=554 nm; g=2.00429) from <u>1h</u> and <u>1i</u>, respectively, were also obtained by a similar method. The possibility that the cation radical locates on the nitrogen atom of 5substituent in <u>1h</u> can be ruled out since the cation radical derived from N,Ndimethylaniline ( Ep=+0.93 V vs. SCE ) has a reported absorption maximum at 460 nm. $^{11,12}$  These cation radicals are relatively inert toward molecular oxygen. The solution of <u>3a</u> was transfered into the suspension of KO<sub>2</sub> as a source of superoxide ion on the vacuum line. The color of the reaction mixture gradually disappeared with gentle evolution of oxygen. The evolved oxygen was measured by a manometer and the reaction mixture was analyzed by hplc. 2-Pyrazoline <u>1a</u> and pyrazole <u>2a</u> were obtained in 60% and 28% yields, respectively, accompanied with comparable amount of oxygen (45%). In spite of the assumption of  $k_{g} \gg k_{r}$  in the singlet oxygenation, back-transfer of an electron is somewhat sluggish in the reaction of the cation radical with superoxide ion. This trend is similar to that phenomena observed in the photosensitized oxygenation via an electrontransfer process; i.e., the formation of the solvent separated cation radical and superoxide pair suppresses a back-transfer process of an electron.<sup>13)</sup> Control experiments show that <u>la</u> is not oxidized to <u>2a</u> with aqueous hydrogen peroxide, and also none of <u>la</u> and <u>2a</u> was detected by quenching of <u>3a</u> with a wet alkaline acetonitrile solution. These observations suggest that both dehydrogenation and annihilation of <u>3a</u> by superoxide ion occured,<sup>5)</sup> as was to the case of the singlet oxygenation of <u>1a</u>.<sup>6)</sup> On the contrary, in treating of <u>3h</u> and <u>3i</u> with  $KO_2$ , the

deprotonation did not take place at all, and interestingly, 93% <u>1h</u> and 91% <u>1i</u> (60% oxygen) were obtained by the annihilation process. These results seem to be in good agreement with those of the singlet oxygenation.<sup>6)</sup>



Fig. UV spectra of 2-pyrazolines, <u>la</u>, <u>lh</u>, and <u>li</u>, and their cation radicals, <u>3a</u>, <u>3h</u>, and <u>3i</u>.

### **Experimental**

Melting points are uncorrected, IR spectra were recorded with a Hitachi 26-50 spectrometer, NMR spectra with a Varian EM 360A spectrometer (solvent, deuteriochloroform; tetramethylsilane as an internal standard), and UV spectra with a Shimazu UV365 spectrometer. Cyclic voltammograms of substrates were obtained in 0.1 M n-Bu<sub>4</sub>NClO<sub>4</sub>/CH<sub>3</sub>CN solution (vs. SCE; scan rate, 200 mV/s; Hokuto Denko Ltd., potentiostat/galvanostat Model HA-301). The one-electron oxidation potentials (Ep) obtained are listed in Table. 2-Pyrazolines <u>la-h</u> were prepared from the corresponding ketones and phenylhydrazine as previously reported.<sup>6,14</sup>) Pyrazoles were prepared from the oxidation of the corresponding 2-pyrazolines with lead tetraacetate.<sup>15)</sup> The physical properties of the 2-pyrazolines and pyrazoles are as follows.

1b: mp 144-145 C;IR(KBr) 1590,1315cm<sup>-1</sup>;UV $\lambda_{max}$ 246nm(logε4.29);Fluorescence 475nm. <sup>1</sup>H NMRδ3.10(dd,1H,J=7.2,18Hz),3.85(dd,1H,J=12.6,18Hz),5.36(dd,1H,J=12.6,7.2Hz), 6.89-7.85(m,14H).Anal Calcd for C<sub>21</sub>H<sub>17</sub>N<sub>2</sub>Cl: C,75.78; H,5.14; N,8.41. Found: C,75.63; N,5.14; N,8.48.

<u>1c</u>: mp 143-145 C;IR(KBr)1590,1320cm<sup>-1</sup>;UV  $\lambda_{max}$  244(loge4.25),355nm(loge4.30); Fluorescence 470 nm;<sup>1</sup>H NMR 62.36(s,3H),3.10(dd,1H,J=7.8,17Hz),3.86(dd,1H,J=12.0, 17Hz),5.26(dd,1H,J=12.0,7.8Hz),6.80-7.77(m.14H);Anal Calcd for C<sub>22</sub>H<sub>20</sub>N<sub>2</sub>: C,84.58; H,6.54; N,8.96. Found: C,84.42; H,6.40; N,8.83.

<u>1d</u>: mp 139.5-141 C;IR(KBr)1590,1320cm<sup>-1</sup>;UV  $\lambda_{max}$ 249(loge4.22)351nm(loge 4.32);Fluorescence 465nm;<sup>1</sup>H NMR 63.09(dd,1H,J=7.2,17Hz),3.85(dd,1H,J=11.4,17Hz), 3.85(s,3H), 5.27(dd,1H,J=11.4,7.2Hz),6.81-7.82(m,14H).Anal Calcd for C<sub>22</sub>H<sub>20</sub>N<sub>2</sub>O: C,80.45; H,6.13; N,8.53. Found C ,80.52; H,6.16; N,8.49.

<u>1e</u>: mp 127-130 C;IR(KBr)1595,1320cm<sup>-1</sup>;UV  $\lambda_{max}$ 225(log ɛ4.32),354nm(log ɛ 4.27);Fluorescence 468nm;<sup>1</sup>H NMR § 3.05(dd,1H,J=7.2,17Hz),3.82(dd,1H,J=11.4,17Hz), 5.23(dd,1H,J=11.4,7.2Hz),6.77-7.80(m,14H). Anal Calcd for C<sub>21</sub>H<sub>17</sub>N<sub>2</sub>Cl: C,75.78; H,5.14; N,8.41. Found: C,75.53; H,5.13; N,8.48.

<u>1f</u>: mp 131-132 C;IR(KBr)1595,1325cm<sup>-1</sup>;UV  $\lambda_{max}$ 240(loge4.23),356nm(log e4.30); Fluorescence 471nm;<sup>1</sup>H NMR & 2.29(s,3H),3.06(dd,1H,J=6.6,17Hz),3.77(dd,1H,12.6, J=17Hz),5.24(dd,1H,J=12.6,6.6Hz),6.80-7.91(m,14H).Anal Calcd for C<sub>22</sub>H<sub>20</sub>N<sub>2</sub>: C,84.58; H,6.45; N,8.96. Found: C,84.38 H,6.47; N,9.06.

<u>1g</u>: mp 119-121 C;IR(KBr)1590,1320cm<sup>-1</sup>;UV  $\lambda_{max}$ 230(log ¢4.38),356nm(log ¢4.31);Fluorescence 471nm;<sup>1</sup>H NMR §3.08(dd,1H,J=7.2,17Hz),3.79(s,3H),3.82(dd,1H,J=12.0,17Hz),5.25(dd,1H,J=12.0,7.2Hz),6.81-7.87(m,14H).Anal Calcd for C<sub>22</sub>H<sub>20</sub>N<sub>2</sub>O: C,80.45; H 6.13; N,8.53. Found: C;80.50; H,6.16; N,8.65.

<u>1h</u>: mp 134-137 C;IR(KBr)1590,1345,1320cm<sup>-1</sup>;UV  $\lambda_{max}$ 255(logε4.44),358nm(logε4.26); Fuorescence 460-490nm(broad);<sup>1</sup>H NMRδ2.95(s,6H),3.10(dd,1H,J=7.2,17Hz),3.82(dd,1H, J=12.6,17Hz),5.23(dd,1H,J=12.6,7.2Hz),6.70-7.92(m.14H).Anal Calcd for C<sub>23</sub>H<sub>23</sub>N<sub>3</sub>: C,80.90; H,6.78; N,12.30. Found: C,80.64; H,6.71; N,12.19.

<u>2b</u>: mp 137-140 C;IR(KBr)3040,1475,1445,1425,760,685cm<sup>-1</sup>;UV $\lambda_{max}$ 258nm(loge4.5); <sup>1</sup>H NMR $\delta$ 6.93(s,1H),7.31-7.69(m,12H),7.91-8.19(m,2H).Anal Calcd for C<sub>21</sub>H<sub>15</sub>N<sub>2</sub>Cl: C,76.24; H,4.57; N,8.46. Found: C,76.01; H,4.63; N,8.46.

 $\frac{2c}{1} \text{ mp } 125-125.5 \text{ C;IR(KBr)}3010,1490,1480,765,755,685 \text{ cm}^{-1};UV\lambda_{max}255 \text{ nm}(\log \epsilon 4.53);$   $\frac{1}{1} \text{ NMR} \delta 2.43(\text{s},3\text{H}), 6.91(\text{s},1\text{H}), 7.21-7.59(\text{m},12\text{H}), 7.90-8.15(\text{m},2\text{H}). \text{Anal Calcd for}$   $C_{22}H_{18}N_2: \text{ C,85.12; H,5.84; N,9.02. Found: C,84.84; H,5.83; N,9.05.}$ 

2d: mp 137-139 C;IR(KBr)1480,1250,1025,840,760,690cm<sup>-1</sup>;UV $\lambda_{max}$ 259nm(loge4.54);<sup>1</sup>H NMR & 3.91(s,3H),6.91(s,1H),7.12(d,2H,J=9.6Hz),7.32-7.59(m,10H),8.04(d,2H,J=9.6Hz). Anal Calcd for C<sub>22</sub>H<sub>18</sub>N<sub>2</sub>O: C,80.95; H,5.55; N,8.58. Found: C,80.79; H,5.54; N,8.60.

 $\frac{2f}{1}: mp 114-115 C; IR(KBr) 3020, 1585, 1485, 1355, 765, 685 cm^{-1}; UV\lambda_{max} 254 nm (log $4.54);$ <sup>1</sup>H NMR \$2.37(s, 3H), 6.8(s, 1H), 7.15-7.65(m, 12H), 7.93-8.18(m, 2H). Anal Calcd for
C<sub>22</sub>H<sub>18</sub>N<sub>2</sub>: C, 85.12; H, 5.84; N, 9.02: Found C, 85.00; H, 5.82; N, 9.08.

2g: mp 76-78 C;IR(KBr)3025,1605,1485,1240,1020,760cm<sup>-1</sup>:UV $\lambda_{max}$  256nm(logε4.58);<sup>1</sup>H NMR δ3.86(s,3H),6.85(s,1H),6.95-7.69(m,12H),7.92-8.17(m,2H).Anal Calcd for C<sub>22</sub>H<sub>18</sub>N<sub>2</sub>O: C,80.95; H,5.55; N,8.58. Found C,80.73; H,5.57; N,8.63.

<u>2h</u>: mp 126.5-129 C;IR(KBr)2880,2800,1605,1490,1445,1360,770 cm<sup>-1</sup>;UV $\lambda_{max}^2$ 273nm (log e4,57);<sup>1</sup>H NMR 63.00(s,6H),6.62-6.92(m,3H),7.13-7.71(m,10H),7.90-8.25(m,2H).Anal Calcd for C<sub>23</sub>H<sub>21</sub>N<sub>3</sub>: C,81.38, H,6.23, N,12.37. Found: C,81.11; H,6.20; N,12.37.

5-Deuterated <u>1a</u> was prepared from the corresponding deuterated chalcone and phenylhydrazine by the procedure for <u>1a</u>.<sup>6,14</sup>) The deuterated chalcone was obtained by Aldol-condensation<sup>14</sup>) of acetophenone and deuterated benzaldehyde obtained from the reduction of benzoyl chloride with lithium tri-t-butoxyalumino deuteride.<sup>16</sup>)

## Rate Measurement in Photosensitized Oxygenation of 2-Pyrazolines

In a typical experiment, <u>1a</u> (0.01 M) with methylene blue (0.2 mM) as a sensitizer were dissolved in 10 ml of methylene chloride and the resulting solution was irradiated with a xenon lamp ( $\lambda > 420$  nm) under an oxygen flow for 10 min. Both <u>1a</u> and <u>2a</u> were analyzed by hplc at an early stage (i.e., 10% conversion). Hplc analysis was performed with a JASCO Trirotar-VI HPLC system, equipped with a 20 cm x 5 mm stainless steel column packed with Finepack SIL C18.

The experiment to determine the  $k_H/k_D$  value was carried out similarly. Photosensitized Oxygenation of 1d and 1h

<u>1d</u>, methylene blue, and dibenzyl ether as an internal standard were dissolved in deuterated chloroform in a NMR tube and the resulting solution was irradiated with a xenon lamp ( $\lambda$ >420 nm) under an oxygen flow for 1 h. None of 1d was observed at all by means of NMR spectroscopy. Under the same condition, <u>1h</u> was recovered in more than 95% yield.

### Formation and Reaction of Cation Radical 3 with Superoxide Ion

In a typical experiment, 2 mmol of <u>1a</u> containing 0.2 mmol of dicyclohexyl 18crown-6, 2 mmol of NOBF<sub>4</sub> and 4 mmol of  $KO_2$  as superoxide ion in acetonitrile were added to the freeze-pump-thaw flask, separately, and the flask was evacuated.<sup>4)</sup> The solution of <u>1a</u> was transfered into the solution of NOBF<sub>4</sub> to give <u>3a</u>. Uv spectra of the cation radicals obtained are shown in Fig. See text for the reaction with superoxide ion.

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