

## Interconversion of Electronic Spin State of *p*-Substituted Arylketocarbene Reactions

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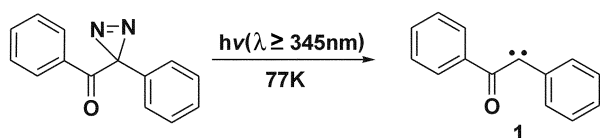
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Rate constants for photolytic reactions of *p*-substituted 2-diazopropiophenones were determined in acetonitrile. The reactions show a comparatively low value of activation energy and activation enthalpy to alkylcarbenes or other arylcarbenes. The transition state corresponds to the step of a new carbonyl bond formation. The high negative  $\rho$ -values are shown in Hammett plots. The kinetics results and EPR spectrum are in accord with a phenomenon that occurs in interconversion between singlet and triplet carbenes.

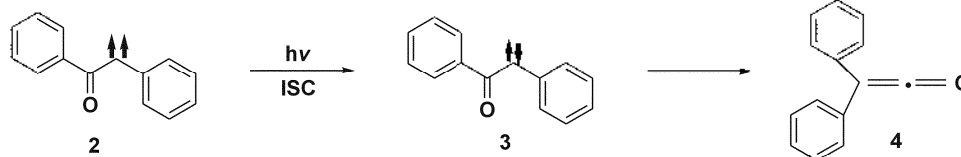
**Key Words :** Arylketocarbenes, Singlet-triplet interconversion, Photolytic rate constant

### Introduction

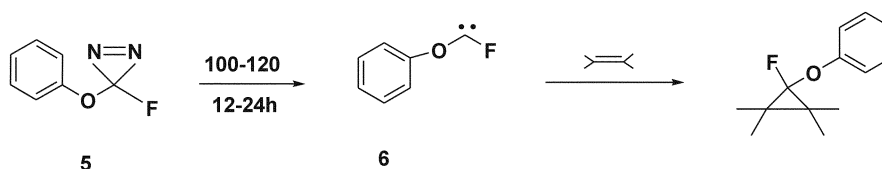
Arylketocarbenes are of interest in the field of reactive carbene intermediates including the Wolff rearrangement reactions.<sup>1-6</sup> Among many arylketocarbenes several benzoylcarbenes have been characterized by matrix EPR spectroscopy.<sup>7</sup> Benzoylphenylcarbene (singlet phenylketocarbene: S-PKC), **1** could be generated by photolysis ( $\lambda \geq 345$  nm) of azibenzil in organic glasses of 2-methyltetrahydrofuran or in powder at 77 K.<sup>8-10</sup>



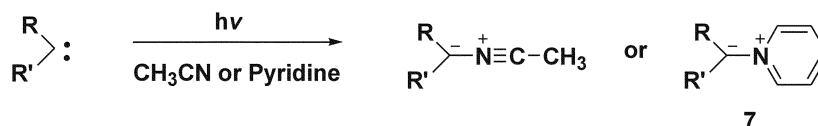
Scheme 1



Scheme 2



Scheme 3



Scheme 4

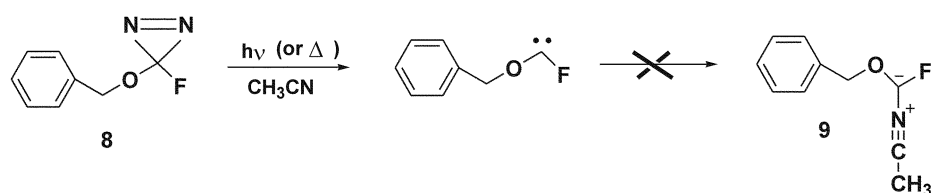
The EPR spectra of benzoylphenylcarbene<sup>8-10</sup> give a good proof related to ketene intermediate, **4** and intersystem crossing (ISC) to the singlet carbene, **3** with subsequent Wolff rearrangement.

Another application of the arylketocarbene, one of benzoyloxycarbenes, fluorophenoxy carbene, **6** is generated by the thermolysis of 3-fluoro-3-phenoxydiazirine, **5** and reacts with a series of alkenes to produce the corresponding cyclopropanes.<sup>11</sup>

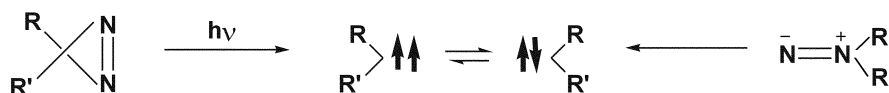
Generally, alkylcarbenes give ylide intermediates, **7** in their trapping compounds as acetonitrile or pyridine.<sup>12-17</sup>

Although many arylketocarbene reactions with acetonitrile or pyridine quenchers have been studied, the ylide intermediates involving arylketocarbene with acetonitrile or pyridine have not yet reported.

The thermolysis or photolysis of benzyloxyfluorodiazirine



Scheme 5



Scheme 6

rine, **8** does not produce ylide intermediate **9**.<sup>11</sup>

The behavior of alkylcarbomethoxycarbene has been reported that is completely different behavior from arylcarbomethoxy carbene.<sup>8-10</sup>

Generally it is well known that photolysis of alkyl carbomethoxy carbene gives a product of triplet sensitization. Triplet sensitization lowers the yield of the product abstracted from singlet carbene as well as the yield of the product of C-H insertion. The C-H insertion product gives a different result as shown a singlet carbene origin, in contrast to the behavior of phenyl carbene and diphenyl carbene. However it is difficult to find a mechanistic approach for electronic state of arylketocarbene.

It is important to identify and understand the true electronic spin state of arylketocarbenes produced from arylketodiazoo compounds. However, most arylketocarbenes were characterized soon after generation from azibenzyl derivatives.<sup>20-22</sup>

Therefore it is necessary to identify a clear-cut photolytic experimental results. Most cases<sup>14,15,23,24</sup> show there are different electronic spin-state in accordance with producing from diazirine derivatives or diazo derivatives as shown in Scheme 6.

A question arises whether the electronic spin state of arylketocarbene changes from singlet origin to triplet within a small energy gap, or prohibit the intersystem crossing along with alternation of the substituents on the phenyl ring. We report here a more detailed reaction mechanism of *p*-substituted phenylketocarbenes based on reactivity involving a singlet-triplet interconversion.

## Experimental Section

**Materials.** *p*-Substituted phenyl- $\alpha$ -diazo ketones (*p*-substituted 2-diazopropiophenones) were synthesized freshly by the literature procedure.<sup>25</sup> A 100 mL, three-neck, round-bottom flask, wrapped with aluminum foil and equipped with a Dean-Stark trap, stir bar, and argon inlet was placed in ice-bath controlled to 0 °C and then was charged with *N*-nitroso-*N*-ethyl urea (0.86 g, 7.34 mmol) and 40 mL of diethyl ether and purged with nitrogen for 20 min. To this were added aqueous KOH solution (10 mL of 40% solution). The mixture was stirred at 0 °C for 30 min.

The reaction mixture was warmed to room temperature and the organic layer was separated from water layer. Sodium hydroxide (2 g) was added into the organic layer and was stirred for 5 min, at 0 °C. Diethyl ether (10 mL) and 0.85 mmol of *p*-substituted benzoyl chloride were added and stirred continuously at 0 °C for 20 hr. The organic layer was washed with petroleum ether and dried. The solvent was removed *in vacuo* to give 0.60 mmol of impure 2-diazopropiophenone of a viscous yellowish red oil, which was purified by medium pressure liquid chromatography using hexane/ethyl acetate (2 : 1) as the eluent to afford 0.52 mmol of pure 2-diazopropiophenone :

***p*-Methoxy-2-diazopropiophenone (*p*-OCH<sub>3</sub>):** IR (KBr) 2972, 2867, 2360, 2070, 1601, 1508, 1343, 1230, 1157, 1002, 839, 565 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.56 (s, 3H), 3.88 (s, 3H), 6.93 (m, 2H), 7.94 (m, 2H).

***p*-Methyl-2-diazopropiophenone (*p*-CH<sub>3</sub>):** IR (KBr) 2975, 2864, 2362, 2068, 1748, 1599, 1341, 1230, 1001, 884 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.40 (s, 3H), 2.59 (s, 3H), 7.25 (m, 2H), 7.86 (m, 2H).

**2-Diazopropiophenone (*p*-H):** IR (KBr) 2977, 2863, 2362, 2073, 1509, 1507, 1341, 1187, 982, 567 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.61 (s, 3H), 7.48 (m, 2H), 7.55 (m, 1H), 7.98 (m, 2H).

***p*-Fluoro-2-diazopropiophenone (*p*-F):** IR (KBr) 2977, 2869, 2362, 2070, 1781, 1749, 1607, 1507, 1343, 638 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.66 (s, 3H), 6.89 (m, 2H), 7.26 (m, 2H).

**Apparatus and Characterization.** The synthesized samples were characterized before using. FT-IR spectra were recorded on a Bruker IFS 55 spectrophotometer. <sup>1</sup>H NMR spectra were measured on a Bruker AC-200 FT, 200 MHz spectrometer and are reported in parts per million downfield from tetramethylsilane. Gas Chromatograph/Mass Spectrometer (GC/MS) analysis was accomplished using a Hewlett-Packard 5890 AX 505 WA with a flame ionization detector and a 30 m  $\times$  0.254 mm ID. DB-1 column. The oven temperature was controlled with the retained time as follows: 70 °C (2 min.) to 180 °C at 10 °C/min., hold 2 min. to 225 °C at 30 °C/min. hold 5 min. Products of the photolysis mixture were isolated by use of either a preparatory thin layer chromatograph or a high performance liquid chromatograph (HPLC). In product isolation the reaction mixtures were concentrated by pumping off most of

the solvent prior to application to the thin layer chromatograph plates. A nitrogen-filled vacuum atmosphere dry box equipped with a dri-train gas purifier was employed for manipulations when the reaction was carried out under anaerobic conditions.

**Kinetics.** Photochemical kinetics were monitored using a Shimadzu UV/Vis-240 spectrophotometer equipped with the Cary sixcell Peltier constant temperature accessory as previously reported.<sup>26-28</sup> A stock solution of *p*-substituted 2-diazo-propiofenone in diethyl ether was injected into a equilibrated acetonitrile for 30 min, and the change in absorbance was followed at 248, 251, 253 and 254 nm for compounds *p*-OCH<sub>3</sub>, *p*-CH<sub>3</sub>, *p*-H, *p*-F, respectively. First-order rate constants for photochemical reactions were determined by a nonlinear least-squares fit to a standard first-order equation. All kinetic runs exhibited exactly first-order behavior for at least 3 half-lives of reaction.

**Low Temperature EPR Spectroscopy.** EPR measurements were made with a Bruker ESP 300F X-band spectrometer as previously reported<sup>27</sup> and *g*-values were calibrated with 2,2-diphenyl-1-picrylhydrazyl using Bruker FRO35M NMR gaussmeter. The sample of *p*-H was 0.30 ml. and were contained in 3-mm cylindrical Suprasil quartz EPR tubes. The samples were sealed under vacuum after three freeze-thaw cycles to remove traces of oxygen and photolyzed for 3-5 min, using 300 or 350 nm lamps. The sample was stored in liquid nitrogen between measurements. The spectrum was obtained at 0.2 G modulation amplitude, a modulation frequency of 100 kHz, and an incident microwave power of 8 mW. The field-frequency lock accessory was operated automatically programmed with automatic frequency control modulation amplitude correction over the attenuation range. Spin concentration measurements were carried out on a dual TE<sub>104</sub> rectangular cavity. 2-Diazopropiofenone was cooled to 77 K in cryogenics (CTI, Helium 99.999% Closed System, R.G.Hansen & Associates Laboratory Cryogenics Systems, Model No. 2561) and photolyzed with 350 nm radiation from a Rayonet Reactor. EPR signals are observed at 2200, 5100 and 6200 G. The triplet EPR spectrum was assigned to yield zero field splitting (*ZFS*) parameters:  $|D/hc| = 0.3120 \text{ cm}^{-1}$  and  $E/hc = 0.0518 \text{ cm}^{-1}$ .

## Results and Discussion

The photochemical reaction of *p*-substituted 2-diazo-

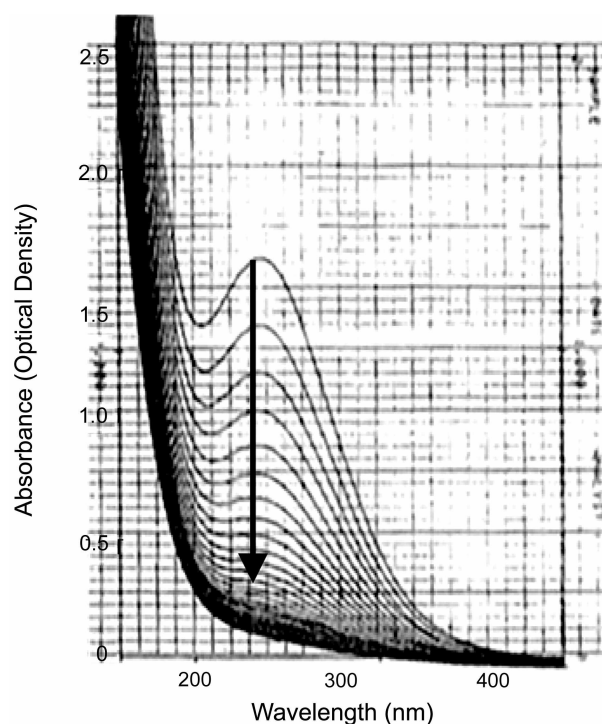
propiofenone (DPP) in acetonitrile (MeCN) were set up at the initial concentrations of  $[DPP] = 1.0 \times 10^{-3} \text{ mol/l.}$  and  $[MeCN] = 3.00 \times 10^{-1} \text{ mol/l.}$  The reaction was followed until the concentration of DPP was decreased to  $1 \times 10^{-5} \text{ mol/l.}$  and then the concentration of MeCN showed to be decreased by  $2.970 \times 10^{-1} \text{ mol/l.}$  The MeCN components of a secondorder reaction remains effectively constant throughout the kinetic runs.

During the reaction occurs, DPP concentration revealed a change of a factor showing 100, and the MeCN concentration changed only a factor showing 1.01.

The observed rate constants are obtained by the following equation (1),<sup>20</sup>

$$\ln \frac{(A_{\infty} - A_0)}{(A_{\infty} - A_t)} = k_{obs} t + \text{constant} \quad (1)$$

where  $A_{\infty}$  is the measurement of optical density at 248 nm (for *p*-OCH<sub>3</sub>) and at the time,  $A_{\infty}$  on the spectrum, and  $A_t$  and  $A_0$  are the measurements of optical density at the time,  $t$

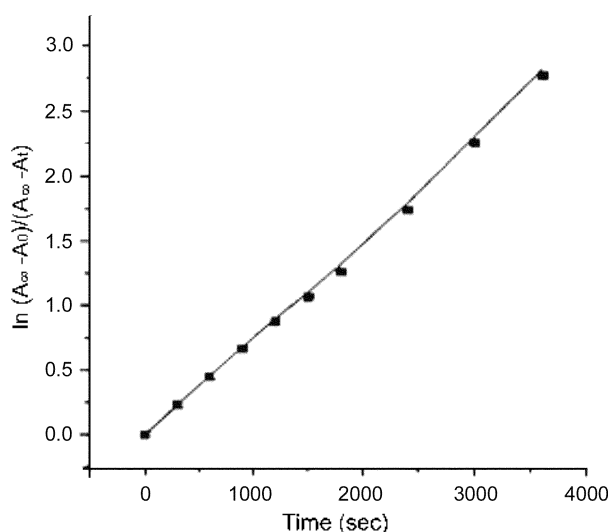


**Figure 1.** The absorption spectra of *p*-methoxy-2-diazopropiofenone in MeCN as a function of reaction time in diethyl ether solution at 313 K ( $\lambda_{max}$ : 248 nm).

**Table 1.** Pseudo First-Order Rate Constants ( $k_{obs} \times 10^4 \text{ sec}^{-1}$ )<sup>a</sup> for the Photochemical Decomposition of *p*-Substituted 2-Diazopropiofenone in MeCN at 313, 323 and 333 K

Temp. (K) <sup>b</sup> (X=)	313	323	333	<i>E<sub>a</sub></i> (kcal/mol)	$\Delta H^\ddagger$ (kcal/mol)	$\Delta S^\ddagger$ (e.u.)	$\Delta G^\ddagger$ (kcal/mol)
<i>p</i> -OCH <sub>3</sub>	148	176	204	3.32	2.68	-58.4	21.5
<i>p</i> -CH <sub>3</sub>	14.3	17.8	21.2	4.08	3.44	-60.6	23.0
<i>p</i> -H	9.11	12.9	16.7	6.28	5.64	-54.4	23.2
<i>p</i> -F	3.50	6.13	8.75	9.50	8.86	-46.0	23.7

<sup>a</sup>Observed rate constants correspond to the average of two independent runs; typical standard deviation is  $\pm 3\%$ . <sup>b</sup>Temp. (K) = (313  $\pm$  0.01) K, (323  $\pm$  0.01) K and (333  $\pm$  0.05) K.



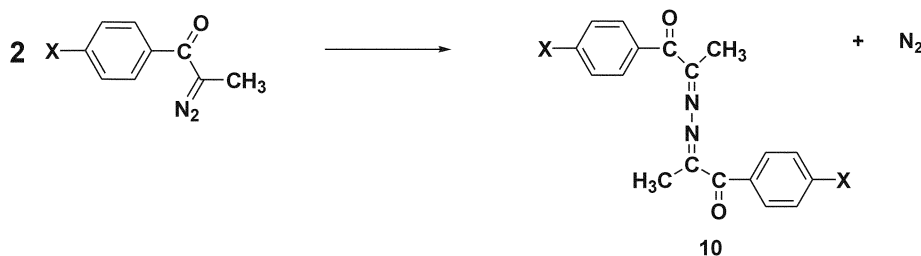
**Figure 2.** Plot of  $\ln(A_{\infty}-A_0)/(A_{\infty}-A_t)$  vs time for the photolytic reaction of *p*-methoxy-2-diazopropiophenone in MeCN at 313 K ( $\lambda_{\text{max}}$ : 248 nm).

and  $t_0$  at the same wavelength. A typical kinetic run using UV/Vis spectrophotometer was shown in Figure 1.

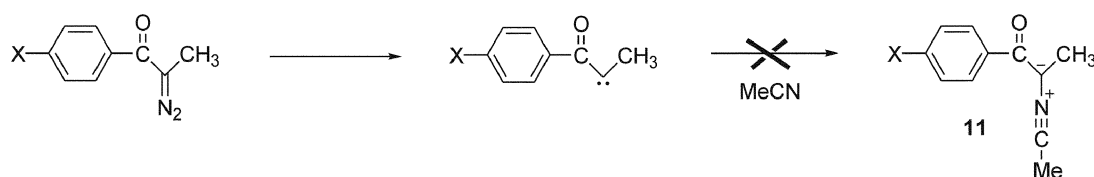
Under the condition given in Table 1, the first-order rate constant of the photochemical reaction of *p*-methoxy-2-diazopropiophenone (DPP) in MeCN was calculated as  $148 \times 10^{-1} \text{sec}^{-1}$  from the data in Figure 2. The observed rate constants,  $k_{\text{obs}}$  are summarized in Table 1, where the activation energy ( $E_a$ ), activation enthalpy ( $\Delta H^\ddagger$ ) and activation Gibbs free energy ( $\Delta G^\ddagger$ ) are also shown.

Generally, the activation enthalpy for decomposition reaction of aryl diazo compounds is known as 3–4 kcal/mol<sup>13</sup> and the activation energy of the essentially diffusion-controlled reaction is 2–3 kcal/mol.<sup>13</sup> The latter value is only an apparent activation energy which results from the decrease in  $k_{\text{diff}}$  at low temperature due to increased solvent viscosity.

The activation enthalpy and the activation energy show



**Scheme 7**



**Scheme 8**

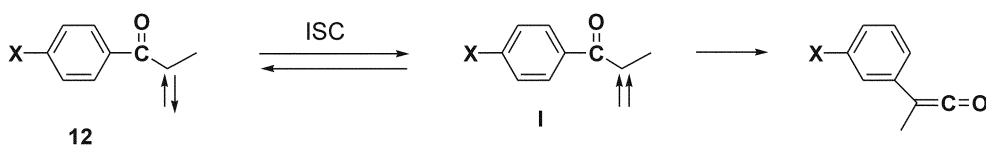
2.68–8.86 kcal/mol and 3.32–9.50 kcal/mol, respectively in Table 1. There is a wide difference in  $E_a$  and  $\Delta H^\ddagger$  between DPP with the electron donating substituents and DPP with the electron withdrawing substituents. Decomposition reactions of DPP with the electron donating substituents are consistent with the diffusion controlled reaction, but those of DPP with the electron withdrawing substituents are in striking contrast to the diffusion-controlled reaction mechanism. If the reactions of DPP with the electron withdrawing substituents do not proceed through the diffusion-controlled reaction, it would expect to produce the azine product (10) before DPP reacts with MeCN as shown in Scheme 7.

It has been reported that the irradiation of typical carbene precursors using lamp or laser such as diphenyl diazomethane or tetraphenylloxirane, can lead to different products and product distributions.<sup>11</sup> However, the irradiation of DPP with MeCN does not give a azine product (10). This seems that the neighboring methyl group in DPP furnishes a steric hindrance at the step of azine formation. If acetonitrile ylide would be produced, then the product of DPP reaction gives an ylide intermediate (11) as shown in Scheme 8.

The reaction was identified for the final product, to find out a possibility to produce azine carefully. However the final product gives only 1-methyl-3-*p*-substituted phenyl-oxirene (MPO) and the acetonitrile ylide was not found in this reaction.

Griller<sup>23</sup> has reported that the azine product comes from the photochemical reaction of diphenyldiazomethane in MeOH. And it shows high activation energy like 5–7 kcal/mol. The result also shows a different tendency that is: the carbene-carbene coupling reaction is in accord with the diffusion-controlled reaction as much as a neglect of the activation energy value.

In this study, it shows low activation energy for the electron donating group and high activation energy for electron withdrawing group as shown in Table 1. This result means that the reaction is involved in a different mechanism which is proceeded by MeOH which has been reported by



Scheme 9

Griller.

Many studies<sup>29,30</sup> reported that carbenes usually produce acetone and nitrile ylides in the case of carbene reaction in acetone or acetonitrile. Therefore it is necessary to examine a possibility for carbene ylide intermediate spectrophotometrically.

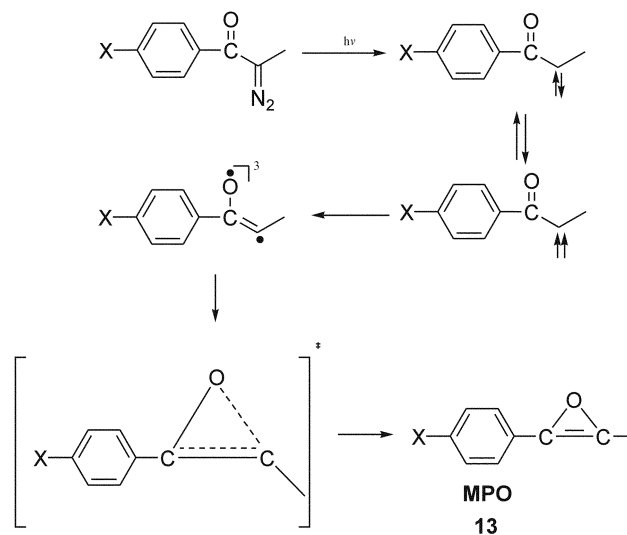
In this reaction we checked the possibility of carbene ylide intermediate using UV/vis spectrophotometer. The result did not show the evidence for acetonitrile ylide intermediate.

The reaction of DPP (*p*-substituted phenyl- $\alpha$ -diazoketone; PDK) in MeCN is achieved in low the activation enthalpy and activation energy as shown in Table 1. This is believed to be an existence of singlet phenylketocarbene (**12**, S-PKC) as shown in Scheme 9. The singlet carbene (**12**) should be produced from the photodecomposition of DPP. Generally, it is well known that ylide intermediate is produced from the triplet phenylketocarbene (**I**, T-PKC).<sup>1-3</sup> It is estimated that the singlet carbene changes to the triplet carbene after intersystem crossing quickly as shown in Scheme 9.

In order to confirm the spin state of the carbene, DPP(*p*-H) was photolyzed in cryogenics at 77 K. The observed EPR spectrum is assigned to triplet carbene which has either a ground triplet state or a triplet state within a few kcal·mol<sup>-1</sup> of the ground state as shown  $|D/hc| = 0.3120$  cm<sup>-1</sup> and  $|E/hc| = 0.0518$  cm<sup>-1</sup>. The value of  $E/D = 0.166$  ( $=0.0518/0.3120$ ) is consistent with the values of typical triplet ketocarbenes.<sup>6</sup> The value of  $E/D$  for ketocarbene produced DPP is similar to those of  $E/D$  of other ketocarbene, for example, as formyl carbene (H-CO- $\dot{C}$ -H) and (CF<sub>3</sub>CO- $\dot{C}$ -CF<sub>3</sub>) perfluoroacetylmethylcarbene as shown as 0.142 and 0.165, however it is a little bit lower than the value of 0.290 for benzoylphenylcarbene (C<sub>6</sub>H<sub>5</sub>CO- $\dot{C}$ -C<sub>6</sub>H<sub>5</sub>).

Photolysis ( $\lambda = 340$  nm  $\pm$  3 nm) of benzoylphenylcarbene, (C<sub>6</sub>H<sub>5</sub>CO- $\dot{C}$ -C<sub>6</sub>H<sub>5</sub>) gives a triplet EPR signals in the corresponding to diazo precursor compound as powder matrix at 77 K as shown as  $|D/hc| = 0.3123$  cm<sup>-1</sup> and  $|E/hc| = 0.0519$  cm<sup>-1</sup>.<sup>6</sup> Upon analysis of the two results of the triplet intermediate at low temperature, 77 K and the singlet intermediate at 313 K  $\sim$  333 K, it is estimated that the two intermediates exist at the early step just after production of the reaction of DPP. The values for benzoylphenylcarbene are close to the value of the ketocarbene, **12** and the result for benzoylphenylcarbene strongly rationalizes that the keto triplet carbene is produced exactly from the photolysis of DPP. It supports the evidence that exists of an intersystem crossing (ISC) to the singlet carbene as shown in Scheme 9.

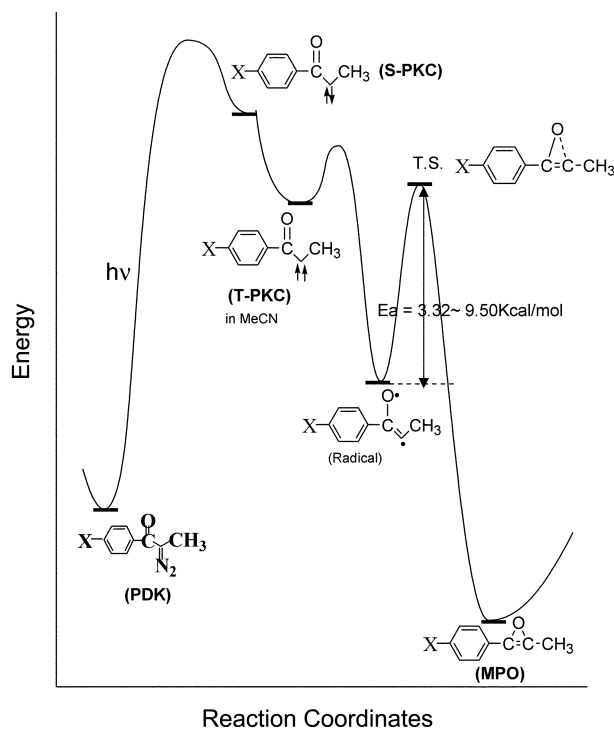
In this research the reaction series, the rate constants are observed at the step of the transition state because the disappearance of the maximum wavelength ( $\lambda_{max} = 253$  nm) for *p*-H is in accord with the formation of the final product



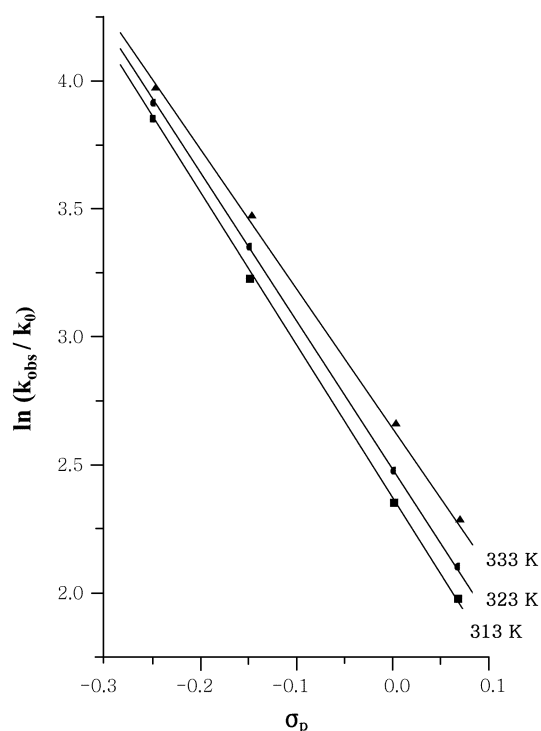
Scheme 10

(MPO, **13**) as shown in Scheme 10.

The product MPO could result to be produced by intramolecular reaction of triplet radicals as shown in Scheme 10.



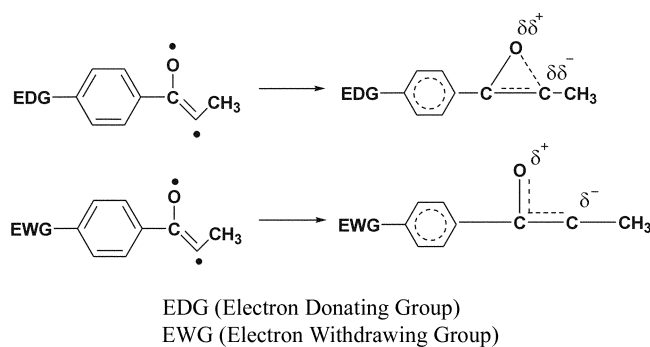
**Figure 3.** Proposed energy surface for the photochemical decomposition reaction of *p*-substituted 2-diazopropiophenone in MeCN.



**Figure 4.** Hammett plots for the photochemical decomposition reaction of *p*-substituted 2-diazopropiophenone in MeCN.

Pople and co-workers<sup>15</sup> have calculated the potential energy surface for reaction of methylene with ammonia. The result for the reaction shows that the potential energy gap between the ylide intermediate and the transition state is 13 kcal/mol and the energy gap between the transition and the final product is 85 kcal/mol. In the reactions of DPP with MeCN the activation energies show in the range of 3.32–9.50 kcal/mol, it indicates a comparatively low value with other carbene reaction.<sup>11</sup> If the triplet radical would be generated as shown in Scheme 10 at the first step, the energy level of the radical should be higher than the energy level of MPO. And a transition state corresponding to C···O bond formation step exists between the radical and MPO. It could be illustrated as shown in Figure 3. The fact that the activation energy which shows a wide range of 3.32–9.50, it infers a conclusion that the transition state is affected strongly by the substituent. For examination of the substituent effect, the logarithms of rate constants were plotted against the substituent constants as shown in the Hammett plot of Figure 4. The high negative  $\rho$ -values show ranging 5.95 ~ -6.12.

It indicates that the reaction of DPP in MeCN is affected largely according to the substituents. That is, in the case of electron donating substituents substituted at the *para*-position of phenyl ring, the electrons in oxygen atom of the C-O· radical would be moving into the right-hand carbon atom of C=C bond and then, it becomes a state of developed bond formation. However, in the case of electron-withdrawing substituents, it presents that the electrons on C-O· radical is barely moved into the right-hand carbon atom of C=C



**Scheme 11**

bond that is a striking contrast to the electronic state of electron-donating substituents.

It is proposed that the transition state corresponds to an appropriate step to make triangle ring in view of the activation parameters (low activation energy and low enthalpy compared with other carbene reactions). A high negative value of  $\rho$  indicates that a positive charge develops at the reaction center, the oxygen atom of carbonyl group in DPP as shown in Scheme 11.

In conclusion, it is shown that the photochemical reactions of *p*-substituted 2-diazopropiophenones (DPP) give the products corresponding to 1-methyl-3-*p*-substituted phenyl-oxirene (MPO). The reactions are achieved in low activation energy and low activation enthalpy. The kinetic data and EPR spectrum are in accord with a phenomenon that occurs in interconversion between singlet carbene and triplet carbene.

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