A Study on the Mechanism for Photochemical Insertion of Methanol Into Aryl Ketocarbenes

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The photochemical reaction mechanism has been investigated for methanol insertion into the *p*-substituted phenylketo carbenes. The triplet spin state of phenyl keto carbene is stabilized by the neighbored carbonyl electrons. When the phenylketo carbene reacts with methanol, the ylied intermediate is formed, then moves to the activated transition state.

**key words:** Methanol insertion, ketocarbene, photochemical reaction

INTRODUCTION

Methanol insertion reaction into the arylketo carbene has been the subject of considerable study to measure the singlet-triplet gap [1]. However many carbenes are only proven possible to detect the triplet ground state by spectroscopic methods and the most low-lying singlet carbenes are not proven to be clear in many cases [2-7].

The singlet carbenes are well known that their empty orbitals react with atoms bearing a lone pair of electrons to form ylids or complexes [8-10].

It is also questionable that the gas phase spectroscopy and a high-level calculation can be applied to the arylketo carbenes to determine values of the singlet-triplet enthalpy. The quenching of a triplet carbene in methanol is the one of the standard method to probe the singlet-triplet energy gap [11-12].

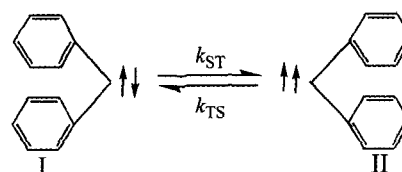The quenching reaction of diphenyl carbene with methanol is well studied by Closs [13] and Bethell [14].
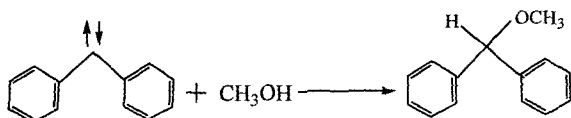
Many chemical evidence for diphenyl carbene is consistent with the rule that spin equilibration ($k_{ST} \rightleftharpoons k_{TS}$) is faster than other reaction processes (III).
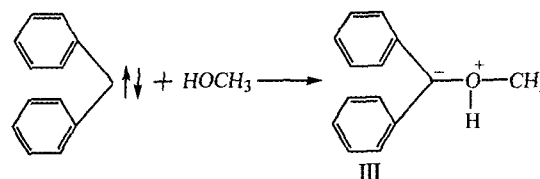

Generally the singlet carbene produces ylid, (III) which can be isolated at low temperature [15].

A different result from a general insight for ylid formation was reported that the quenching reaction of diphenyl carbene with *tert*-butyl alcohol [16]; the ylid forming step of diphenyl carbene with *tert*-butyl alcohol may proceed *via* a reversible reaction.

Even though the kinetic and spectroscopic data are consistent with the reversible reaction mechanism, the energetic problem remains unconvinced. The reverse reaction appears to be prohibited energetically in the case of singlet carbene chemistry [17-18]. If the arylketo carbenes react with methanol they would show a sharp distinction phenomenon because the arylketo carbenes bear ketocarbon atom neighbored with the reaction center.

We report here with a more detailed and new reactivity and reaction mechanism of *p*-substituted phenyl ketocarbenes involving a singlet-triplet conversion.
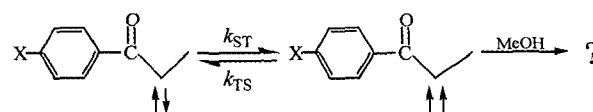
MATERIALS AND METHODS

p-Substituted phenyl-α-diazoketones (2-diazopropiophenones) were synthesized freshly by the literature procedure [19]. A 100mL, three-neck, round-bottom flask, wrapped in aluminum foil and equipped with a Dean-Stark trap, stir bar, and argon inlet was placed in ice-bath controlled to 0°C then was charged with N-nitroso-N-ethyl urea (0.86g, 7.34m mol) and 40mL of diethyl ether and then sparged with nitrogen for 20min. To this were added aqueous KOH solution (10mL 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 (2g) was added into the organic mixture layer and was stirred for 5 min. at 0 °C. Diethyl ether (10mL) and 0.85mmol of p-substituted benzoyl chloride were added and stirred continuously at 0°C for 20hr. The organic layer was washed with petroleum ether and dried, the solvent was removed in vacuo to give 0.60 mmol of 2-diazopropiophenone of a viscous yellow red oil, which was purified via medium pressure liquid chromatography [hexane/ethyl acetate(2:1)] to afford 0.52 mmol of 2-diazopropiophenone : p-methoxy-2-diazopropiophenone ; IR(KBr) 2972, 2867, 2360, 2070, 1601, 1508, 1343, 1231, 1157, 1002, 839, 565cm^{-1} ; ^{1}H NMR (ppm, CDCl$_3$) δ2.56(s, 3H), 3.88(s, 3H), 6.93(m, 2H), 7.94(m, 2H). p-methyl-2-diazopropiophenone ; IR(KBr) 2975, 2864, 2362, 2068, 1748, 1599, 1341, 1230, 1001, 884 cm^{-1} ; ^{1}H NMR(ppm, CDCl$_3$) δ2.40(s, 3H), 2.59(s, 3H), 7.25(m, 2H) 7.86(m, 2H). 2-diazopropiophenone ; IR(KBr) 2977, 2863, 2362, 2073, 1509, 1507, 1341, 1187, 982, 567cm^{-1}; ^{1}H NMR (ppm, CDCl3) δ2.61(s,3H), 7.48(m,2H) 7.55(m,1H), 7.98(m,2H). p-fluoro-2-diazopropiophenone ; IR(KBr) 2977, 2869, 2362, 2070, 1781, 1749, 1601, 1507, 1343, 638cm^{-1}; ^{1}H NMR (ppm, CDCl$_3$) δ2.66(s,3H), 6.89(m, 2H), 7.26(m, 2H). A nitrogen-filled Vacuum Atmospheres drybox equipped with a Dri-Train gas purifier was employed for manipulations when the reaction was carried out under anaerobic conditions. ^{1}H-NMR spectra were recorded on a Bruker AC-200MHz spectrometer using CDCl$_3$ as a slovent. IR spectra were recorded on a Bruker IFS-55 spectrophotometer.

KINETICS

Photochemical kinetics were monitored using a Shimadzu UV/vis-240 spectrophotometer equipped with the Cary six-cell Peltier constant temperature accessory. A stock solution of p-substituted 2-diazo-propiophenone in dietheyl ether was injected into a equilibrated methanol for 30 min. and the change in absorbance was followed at 248, 251, 253 and 254nm for compounds p-OCH$_3$, p-CH$_3$, 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 cleanly first-order

behavior for at least 3 half-lives of reaction.

RESULTS AND DISCUSSION

The photochemical reaction of p-substituted 2-diazopropiophenone(DPP) with methanol (MeOH) were set up at the initial concentrations of [DPP] = 1.0×10^{-3}mol/L and [MeOH] = 3.000×10^{-1}mol/L. The reaction was followed until the concentration of DPP was decreased to 1×10^{-5}mol/L, and then the concentration of methanol showed to be decreased 2.970 $\times 10^{-1}$mol/L. The methanol components of a second-order reaction remains effectively constant through the kinetic runs. During the reaction occurs DPP concentration change of a factor shows 100, in contrast to the methanol concentration change of a factor shows 1.01. The second-order rate equation for the reaction of DPP with MeOH follows

$$- \frac{d[DPP]}{dt} = k_2 \, [DPP][MeOH] \qquad (1)$$

Equation (1) can be rewritten as follows since [MeOH] is almost constant during the reaction occurs.

$$- \frac{d[DPP]}{dt} = k_{obs} \, [DPP] \qquad (2)$$

where, $k_{obs} = k_2 \, [MeOH]$ (3)

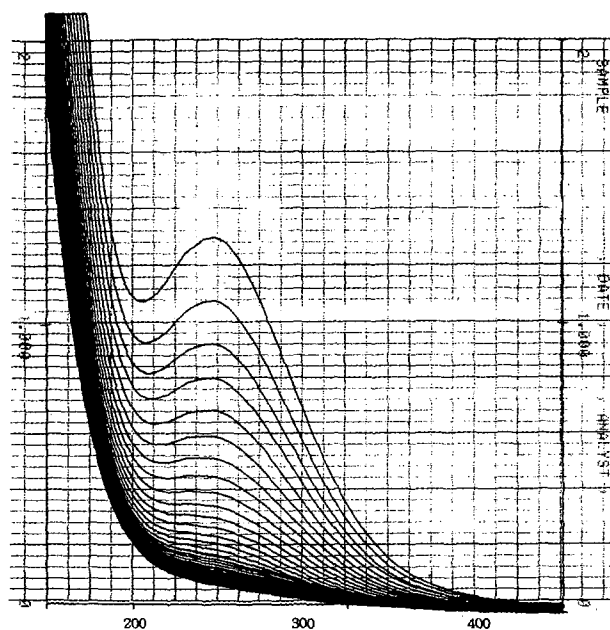The observed rate constants are obtained by the following equation (4).[20]

Figure 1. The spectra of p-methyl-2-diazopropiophenone with methanol as a function of reaction time in diethyl ether solution at 313K (λmax : 250nm).

Table 1. Pseudo First-Order Rate Constants($k_{obs} \times 10^4$ ·sec⁻¹) for the Photochemical Decomposition of p-Substituted 2-diazopropiophenone with MeOH at 313, 323 and 333K

X= \ Temp.(K)	313	323	333	Ea (kcal/mol)	$\Delta H^{\neq}$ (kcal/mol)	$\Delta G^{\neq}$ (kcal/mol)
p-OCH₃	97.3	107	118	2.00	1.37	21.2
p-CH₃	11.8	13.1	14.9	2.47	1.84	22.5
p-H	2.25	2.56	3.16	3.39	2.77	23.6
p-F	1.07	1.35	1.63	4.19	3.57	24.0

$$\ln \frac{(A_\infty - A_o)}{(A_\infty - A_t)} = k_{obs} + constant \tag{4}$$

where A_∞ is the measurement of optical density at 250nm and at the time, t_∞ on the spectrum, and A_t and A_o are the measurements of optical density at the time, t and t_o at the same wave length. 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-methyl-2-diazopropiophenone (DPP) with MeOH at 313K was calculated as 11.8×10^{-4} sec⁻¹ based on the data in Figure 2. The observed rate constants, k_{obs} are summarized in Table 1, where the activation energy (E_a), activation enthalpy ($\Delta H^\dagger$) and activation Gibbs free energy ($\Delta G^\dagger$) are also shown.

Generally, the activation enthalpy for decomposition reaction of aryl diazo compounds is known as 3-4 kcal/mol [21] and the activation energy of the essentially diffusion-controlled reaction is 2~3 kcal/mol [21]. The latter value is only an
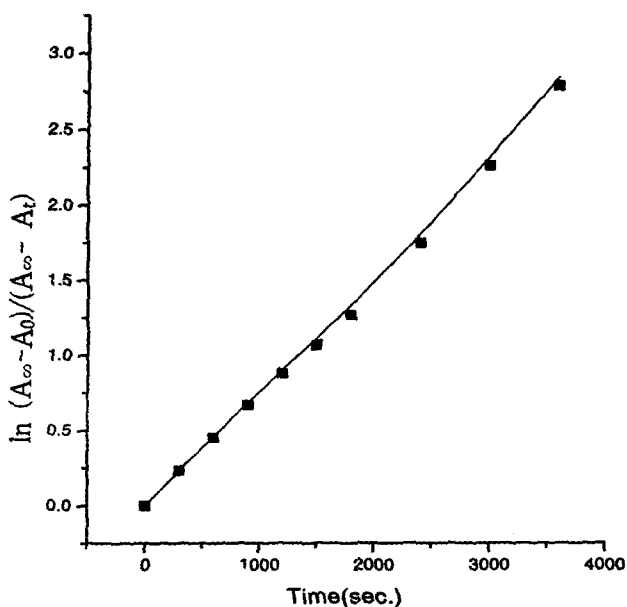

Figure 2. Plot of ln $\frac{(A_\infty - A_t)}{(A_\infty - A_t)}$ vs. time for the photolytic reaction of p-methyl-2-diazopropiophenone with methanol in diethyl ether solution at 313K (λ_{max} : 250nm).

apparent activation energy which results from the decrease in k_{diff} at low temperature due to increased solvent viscosity.

The activation enthalpy and the activation energy show 1.37~3.57 kcal/mol and 2.00~4.19 kcal/mol, respectively in Table 1. There is a wide difference between the electron donating substituent and the electron withdrawing substituent on DPP. The electron donating substituent is consistent with the diffusion-controlled reaction, but the electron withdrawing substituent is in striking contrast to the diffusion-controlled reaction mechanism. If the reaction path of the electron withdrawing substituent does not proceed through the diffusion-controlled reaction, it would expect to produce the azine product (IV) before DPP reacts with MeOH as shown in equation (5).
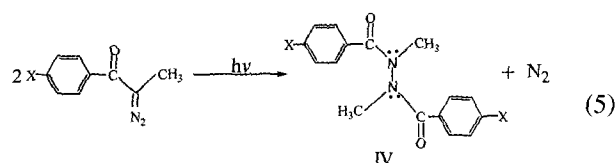

It has been reported that the irradiation of typical carbene precursors using lamp or laser such as diphenyl diazomethane or tetraphenyloxirane, can lead to different products and product distributions [22]. However, the irradiation of DPP with MeOH did not give a azine product (IV).

This seems that the neighbored methyl group with diazo group in DPP furnishes a steric hinderance at the step of azine forming.

The reaction of DPP with MeOH gives p-substituted 2-methoxypropiophenone (MPP) as a final product. It is attributed that the product of MPP should proceed through a ylid intermediate (VI) as shown in Scheme 1. The reaction mechanism as shown in Scheme 1 is analogized the whole reaction path out of the identification of the final product (MPP) and the result of exclusion of possibility to produce azine.

Griller [23] has reported that the azine product gives from the photochemical reaction of diphenyldiazomethane in MeOH and observed a high activation energy like 5~7kcal/mol, however the carbene-carbene coupling reaction is in accord with the diffusion-controlled reaction as much as a neglet of the activation energy value. The reaction of DPP with MeOH is resulted in very low the activation enthalpy and activation energy as shown in Table 1. This is believed an existence of singlet carbene (V) as shown in Scheme 1.

The singlet carbene (V) should be produced from the photo decomposition of DPP. Generally, it is well known that ylid intermediate is produced from the triplet carbene [1-3]. It is forecasted that the singlet carbene changes to the triplet carbene after intersystem crossing quickly as shown in Scheme 1. In this research the reaction series the rate constants are observed at the step of final product (MPP) forming because the disappearance of the maximum wave length (λmax) is

Scheme 1
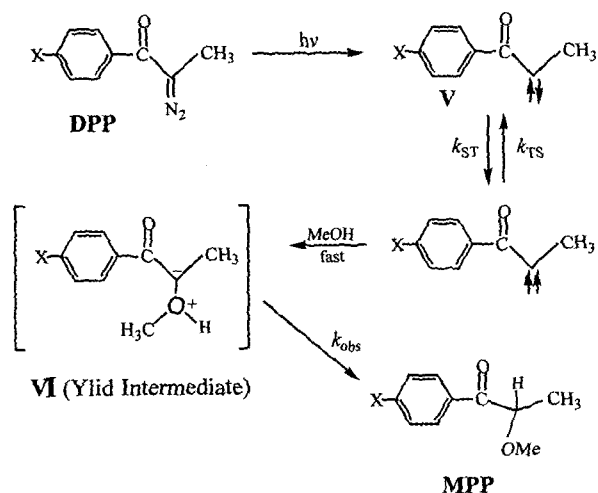
in accord with the forming of final product (MPP). In comparison with the ylid intermediate and the final product (MPP), a transition state should be in existence between the intermediate and the product. The transition state would be a proton migration step as shown in Scheme 2 based on the assumption for an existence of transition state.

Scheme 2
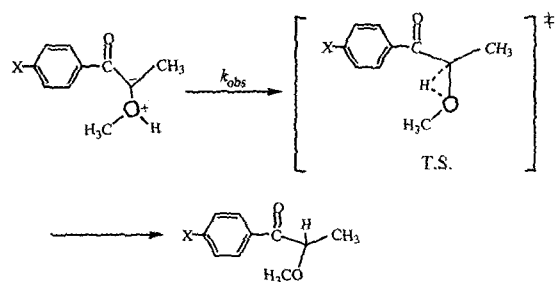
Pople and co-workers [24] have calculated the potential energy surface for reaction of methylene with ammonia. The results for the reaction shows that the potential energy gap between the ylid intermediate and the transition state is 13kcal/mol and the energy gap between the transition and the final product is 85kcal/mol.

In the reactions of DPP with MeOH the activation energies, 2.00 ~ 4.19kcal/mol indicate a very narrow gap compared with other carbene reactions [24].

The energy gap between the ylid intermediate and transition state can be shown as shown in Figure 2. It is predicted to form a kind of acetophenone dimer (V) as shown in Figure 3 if the reaction would proceed only through the singlet carbene (I).

The product of acetophenone dimer did not produce from the product analysis. If the acetophenone dimer was produced, the reaction would occurs through a different reaction coordinate (I→V) as is the case of diffusion-controlled reaction,
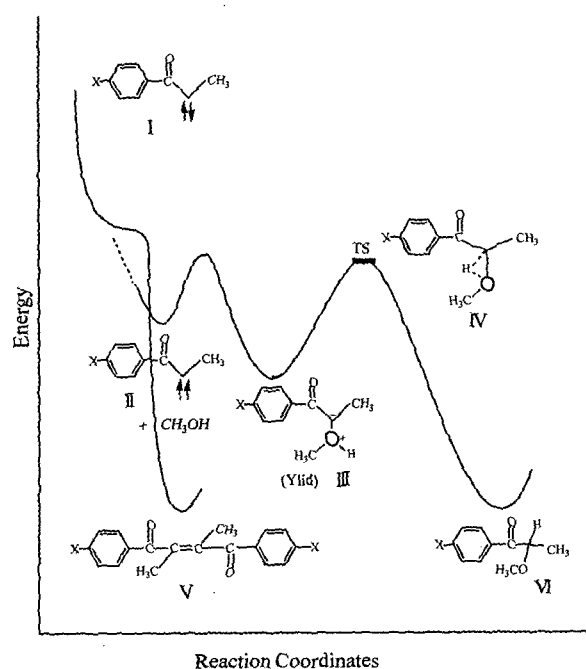

Reaction Coordinates

Figure 3. Proposed energy surface for the photochemical decomposition of p-substituted 2-diazopropiophenone with methanol in the case of involving the reaction of diffusion controlled with singlet state carbene.

as shown in Figure 3. In conclusion, the photochemical reaction of DPP with MeOH proceeds through the ylid intermediate and the transition state of hydrogen migration state. The singlet carbene is produced from DPP directly then, it is conversed quickly into the triplet carbene.

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