

# A Simple Hückel Approach to Intramolecular Photocyclization Reaction of N-(2-Chlorobenzyl)-Pyridinium, N-(Benzyl)-2-Chloropyridinium, and N-(2-Chlorobenzyl)-2-Chloropyridinium Salts

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We have calculated the  $\pi$ -electron density, atom self-polarizability, and free valence on each atom of N-(2-chlorobenzyl)-pyridinium, N-(benzyl)-2-chloropyridinium, and N-(2-chlorobenzyl)-2-chloropyridinium salts using a simple Hückel method in order to discuss their intramolecular photocyclization reaction in a qualitative method. Our calculation qualitatively predicts that photocyclization occurs through forming radicals as a reaction intermediate by breaking a C-Cl bond after photoexcitation into a triplet state via intersystem crossing from an initially excited singlet state. We noticed that this C-Cl bond breaking is aided by  $\pi$ -complex formation between a chlorine atom and the  $\pi$ -electrons of the neighboring ring in the triplet state and a stronger  $\pi$ -complex bond makes C-Cl bond breaking, *i.e.*, radical formation, much easier. A chlorine atom will form a stronger  $\pi$ -complex bond to a benzyl ring of N-(benzyl)-2-chloropyridinium than a pyridinium ring of N-(2-chlorobenzyl)-pyridinium because the former can donate its  $\pi$ -electron more easily than the latter. The chlorine at position 15 of N-(2-chlorobenzyl)-2-chloropyridinium salt in the excited state also provides its  $\pi$ -electron to the benzyl ring. So this  $\pi$ -electron can increase the bond strength of the  $\pi$ -complex. Therefore, the strength of  $\pi$ -complex follows the order of N-(2-chlorobenzyl)-2-chloropyridinium, N-(benzyl)-2-chloropyridinium, and N-(2-chlorobenzyl)-pyridinium salts and thus the radical formation rate. This provides us with an intramolecular photocyclization reaction rate of the same order as given above.

## Introduction

There has been much interest in the reaction mechanism of intramolecular photocyclization of N-(halobenzyl)-halopyridinium salts, but a few experimental studies including photochemical reaction<sup>1</sup> and time resolved spectroscopy<sup>2</sup> have been performed, which are not enough to satisfactorily establish the intramolecular photocyclization mechanism. No theoretical study in this field has been performed so far. Thus a theoretical approach would be valuable.

When the compounds were irradiated with ultraviolet light, the photocyclization was observed. It was experimentally verified that the photocyclization was followed by intersystem crossing between the excited singlet and triplet states. That is, the photocyclization did not occur when the oxygen molecule, the well-known triplet quencher, existed. This implied that mainly the triplet states participate in the reaction.<sup>1</sup>

Grimshaw and de Silva proposed it includes  $\pi$ -complex before a ring formation.<sup>3</sup> Park *et al.* later proposed two possible  $\pi$ -complexes, *i.e.*, a tight  $\pi$ -complex and a loose  $\pi$ -complex, in the reaction path after the intersystem crossing.<sup>1</sup> He described the tight  $\pi$ -complex as a halogen atom of the pyridinium ring bound to a benzene ring through a strong  $\pi$ -complexation, and the loose  $\pi$ -complex, a hydrogen atom of the benzene ring bound to a pyridinium ring through weak  $\pi$ -complexation. He suggested that the tight one should provide more quantum yields, *i.e.*, a higher reaction rate.

Our recent experiment showed that the reaction involved radicals. In this experiment, transient absorptions were observed for three radicals, halogen anion, free phenyl, and conjugated pyridinium radicals.<sup>2</sup> The results indicate that the reaction mechanism should involve the radicals as reaction intermediates. There also have been many other works which report radical intramolecular photocyclization reac-

tions.<sup>7-15</sup>

Here, we performed a simple Hückel calculation in order to discuss the photocyclization reaction in a qualitative way with the  $\pi$ -electron density, atom self-polarizability, and free valence on each atom of the N-(2-chlorobenzyl)-pyridinium, N-(benzyl)-2-chloropyridinium, and N-(2-chlorobenzyl)-2-chloropyridinium salts, respectively. The experimentally observed ratio of rate constant of the above three compounds in the same order as above is 1 : 2.2 : 6.1. The above three calculated values will be used to qualitatively discuss the relative photocyclization rate. Although the present calculation is so simple, the results explain the observed relative photocyclization reaction rates qualitatively well and may help finding the correct mechanism.

## Calculations

All calculations were performed using the simple Hückel method.<sup>4</sup> The simple Hückel method has been widely used in  $\pi$ -bonded organic molecules. Although the calculation is so simple, the results are qualitatively well consistent with the experimental ones and thus it has been one of the major tools for organic chemists when they tried to explain their experimental results from a theoretical perspective. This qualitative agreement should result from the usage of the experimental parameters,  $\alpha$  and  $\beta$  in the calculation which are defined as,

$$\langle i|H|i\rangle = H_{ii} = \alpha$$

$$\langle i|H|j\rangle = H_{ij} = \beta \text{ if } i \text{ is bonded to } j \\ 0 \text{ otherwise} \quad (1)$$

respectively, where  $H$  is the Hückel Hamiltonian whose exact form need not be defined since the experimental parameters

**Table 1.** Values used for  $h$  and  $k$  parameters

	$h$	$k$
N <sup>+</sup>	2.0	1.0
Cl	2.0	0.4
Methylene <sup>a</sup>	-0.5	0.0

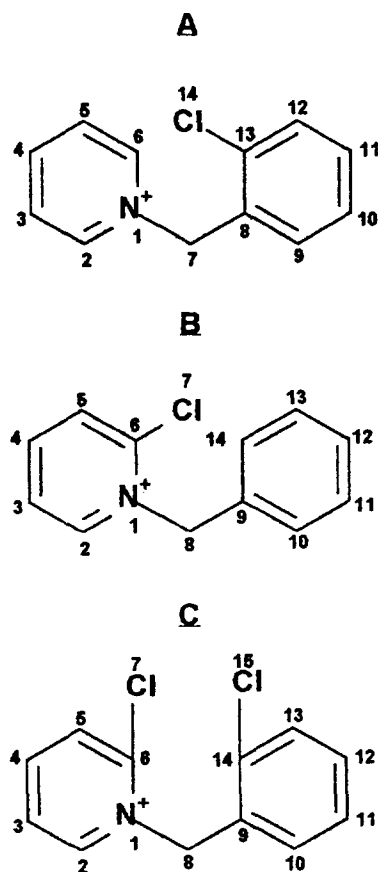
<sup>a</sup>A bridge carbon atom between benzyl and pyridinium rings.

**Table 2.**  $\pi$ -electron density ( $q_r$ ), atom self-polarizability ( $\pi_{rr}$ ), and free valence ( $F_r$ ) for the  $r$ th-carbon atom which participates in the photocyclization reaction<sup>a</sup>

		$q_r$	$\pi_{rr}$	$F_r$	
A <sup>b</sup>	C <sub>2</sub>	$\pi$	0.7592	-0.4192	0.5151
	(or C <sub>6</sub> )	$\pi^*$	0.7518		
	C <sub>13</sub>	$\pi$	0.9879	-0.3914	
		$\pi^*$	0.6768		
	N <sup>+</sup>	$\pi$	1.6219		
		$\pi^*$	1.7763		
B <sup>b</sup>	C <sub>6</sub>	$\pi$	0.7506	-0.4022	0.3987
		$\pi^*$	0.7561		
	C <sub>10</sub>	$\pi$	1.0	-0.3982	
	(or C <sub>14</sub> )	$\pi^*$	1.0		
	N <sup>+</sup>	$\pi$	1.6288		
		$\pi^*$	1.7789		
C <sup>b</sup>	C <sub>6</sub>	$\pi$	0.7506	-0.4022	0.3983
		$\pi^*$	0.7561		
	C <sub>10</sub>	$\pi$	0.9995	-0.3979	
		$\pi^*$	1.1788		
	N <sup>+</sup>	$\pi$	1.6288		
		$\pi^*$	1.7789		
	Cl <sub>15</sub>	$\pi$	1.9849		0.1632
		$\pi^*$	1.9377		
	Cl <sub>14</sub>	$\pi$	0.9879	-0.3914	
		$\pi^*$	0.6768		

<sup>a</sup>Subscripts on carbon, chlorine, and N<sup>+</sup> atoms indicate position of atoms presented in Figure 1. <sup>b</sup>A is N-(2-chlorobenzyl)-pyridinium salt, B is N-(benzyl)-2-chloropyridinium salt, and C is N-(2-chlorobenzyl)-2-chloropyridinium salt. <sup>c</sup>When  $q_r$  is smaller than 1.0, the  $r$ th-carbon atom possesses positive polarity, when bigger than 1.0, it possesses negative one, and when 1.0, it is neutral.

$\alpha$  and  $\beta$  are used. Each structure of N-(2-chlorobenzyl)-pyridinium, N-(benzyl)-2-chloropyridinium, and N-(2-chlorobenzyl)-2-chloropyridinium salts with their atom number are presented in Figure 1-(A), -(B), and -(C), respectively. The  $\alpha^*$  and  $\beta^*$  for each nitrogen, chlorine, and methylene carbon atoms are corrected such that  $\alpha^* = \alpha + h\beta$  and  $\beta^* = k\beta$  where  $\alpha$  and  $\beta$  are the parameters for carbon atoms on the benzyl and pyridinium rings. The  $h$  and  $k$  values are provided in Table 1. The determinants can be divided into two parts because the methylene carbon between benzyl and pyridi-

**Figure 1.** Schematic diagrams of N-(2-chlorobenzyl)-pyridinium (A), N-(benzyl)-2-chloropyridinium (B), and N-(2-chlorobenzyl)-2-chloropyridinium (C) salts.

nium rings does not pass the  $\pi$ -electrons. This implies that the two rings may be treated as independent of each other.

The concerned carbon atoms which participate in the reaction are here carbon atoms at position 2, 6, and 13 of N-(2-chlorobenzyl) pyridinium salt, carbon atoms at position 6, 10, and 14 of N-(benzyl)-2-chloropyridinium, and carbon atoms at position 6 and 10 of N-(2-chlorobenzyl)-2-chloropyridinium salt, referring to the experimental results.<sup>1</sup> The results of  $\pi$ -electron density, atom self-polarizability, and free valence on these atoms are presented in Table 2.

## Results and Discussion

It was experimentally observed that intramolecular photocyclization occurred by forming a bond between a carbon atom at position 2 (or 6, both are equivalent) and a carbon atom at position 13 of N-(2-chlorobenzyl)-pyridinium salt, a carbon atom at position 6 and a carbon atom at position 10 (or 14, both are equivalent) of N-(benzyl)-2-chloropyridinium, and a carbon atom at position 6 and a carbon atom at position 10 of N-(2-chlorobenzyl)-2-chloropyridinium salt and the measured relative photocyclization rate was 1 : 2.2 : 6.1.

It is reasonable to assume that the structural effect is the same for all of the compounds as can be imagined from their two dimensional figures presented in Figure 1. Although there are three possible transitions, *i.e.*,  $\pi$  to  $\pi^*$ ,  $\pi$

to  $\sigma^*$ , and  $n$  to  $\pi^*$  transitions when they are irradiated with UV photon, we consider there only one  $\pi^*$  excited state in this study because the observed large extinction coefficient of absorption of the pyridinium salts indicates this transition. The  $\sigma^*$  state had been recently assigned by Takemura and his coworkers from their phosphorescence spectra of halogenated benzenes.<sup>5,6</sup> Thus  $\pi$  to  $\sigma^*$  transition needs to be included to discuss the photoreaction more accurately. We also assume that the  $\pi$ -complex model<sup>1,3</sup> is applicable to the compounds considered here. The  $\pi$ -complexation aids radical formation because it weakens the C-Cl bond and thus facilitates C-Cl bond breaking.

The radical reaction rate largely depends on both the free valence value of the attacked carbon atoms and the ease of radical formation. The latter is related to the strength of the  $\pi$ -complex. When there are several possible carbon atoms to be attacked by a radical, then the radical goes to the carbon atom with the largest free valence value. In the present compounds, there are two possible carbon atoms to be attacked, which are carbon atoms at position 2 and 6 (both are equivalent) of N-(2-chlorobenzyl)-pyridinium salt, carbon atoms at position 10 and 14 (both are also equivalent) of N-(benzyl)-2-chloropyridinium salt, and carbon atoms at position 10 and 14 or carbon atoms at position 2 and 6 of N-(2-chlorobenzyl)-2-chloropyridinium salt as can be seen in Figure 1. We will qualitatively consider the photocyclization reaction for each compound separately.

Considering the reaction of N-(2-chlorobenzyl)-pyridinium salt, the  $\pi$ -electron charge of the pyridinium ring is drawn into  $N^+$  in the ground  $\pi$  and excited triplet  $\pi^*$  states (see Table 2). The chlorine atom at position 14 gives away its  $\pi$ -electron to benzyl ring by 0.04 when it is photoexcited. Thus it would draw a  $\pi$ -electron through  $\pi$ -complexation from the pyridinium ring. However, the pyridinium ring can not efficiently provide its  $\pi$ -electron to the chlorine atom because it is a poor electron donor. Thus, the  $\pi$ -complex would be relatively very weak and so the bond between carbon atoms at position 13 and 14 is not much weakened and radical formation is not much aided by formation of the  $\pi$ -complex. Once a radical carbon atom at position 13 is formed, photocyclization readily proceeds through radical attack to carbon atom at position 2 or 6 both of which possess large free valence and atom self-polarizability, respectively. Geometry allows the radical carbon atom at position 13 to attack only the carbon atom at position 2 or 6. Thus intramolecular photocyclization occurs slowly, which is limited by radical formation.

In photocyclization of N-(benzyl)-2-chloropyridinium salt, the benzyl ring can provide the chlorine atom with its  $\pi$ -electron more easily than the pyridinium ring of N-(2-chlorobenzyl)-pyridinium salt. So N-(benzyl)-2-chloropyridinium salt forms a stronger  $\pi$ -complex than N-(2-chlorobenzyl)-pyridinium salt. This stronger  $\pi$ -complex allows radicals to form more easily. Therefore, the photocyclization reaction of N-(benzyl)-2-chloropyridinium salt is faster than N-(2-chlorobenzyl)-pyridinium salt.

N-(2-chlorobenzyl)-2-chloropyridinium salt reacts fastest among the three compounds according to the experimental observation.<sup>1</sup> This means that this compound makes radicals most easily. As mentioned before, the chlorine atom at position 15 adds its  $\pi$ -electron to benzyl ring by 0.04 when the

benzyl ring is excited and so the benzyl ring can donate its increased  $\pi$ -electron to the chlorine atom at position 7. Therefore, N-(2-chlorobenzyl)-2-chloropyridinium salt forms the strongest  $\pi$ -complex and makes a radical most easily among the three compounds. Once a radical on carbon atom 6 is formed, it can attack the carbon atom at position 10 or 14. However, the carbon atom at position 10 has larger a free valence (0.3983) than the carbon atom at position 14 (0.1632) with similar atom self-polarizabilities, respectively, the radical on the carbon atom at position 6 attacks the carbon atom at position 10 rather than at position 14, which is consistent with the experimental results.<sup>1</sup>

## Conclusion

We have calculated the  $\pi$ -electron charge density, atom self-polarizability, and free valence of N-(2-chlorobenzyl) pyridinium, N-(benzyl)-2-chloropyridinium, and N-(2-chlorobenzyl)-2-chloropyridinium salts, respectively in order to discuss their intramolecular photocyclization reaction in a qualitative way using a simple Hückel method.

We found that the photocyclization rate is governed by the ease of radical formation. If we assume that reaction proceeds through  $\pi$ -complexation, which is a bond between a Cl atom and  $\pi$ -electrons of the neighboring ring, the radical formation is aided by  $\pi$ -complexation. Here, the stronger  $\pi$ -complex bond makes radical formation easier because it makes the carbon-chlorine bond weaker and thus can break this bond easily to make radicals.

A chlorine atom will form a stronger  $\pi$ -complex bond to the benzyl ring (N-(benzyl)-2-chloropyridinium case) than the pyridinium ring (N-(2-chlorobenzyl)-pyridinium case) because the former can donate its  $\pi$ -electron to a chlorine atom more easily than the latter. The chlorine atom at position 15 of N-(2-chlorobenzyl)-2-chloropyridinium salt in the excited state also provides its  $\pi$ -electron to the benzyl ring. So this added  $\pi$ -electron further increases the strength of its  $\pi$ -complex bond. Therefore, since a stronger  $\pi$ -complex bond produces radicals much more easily, the radical formation rate follows the order of N-(2-chlorobenzyl)-2-chloropyridinium, N-(benzyl)-2-chloropyridinium, and N-(2-chlorobenzyl)-pyridinium salts. Thus this provides us with the order of relative intramolecular photocyclization reaction rate as given above.

However, it should be emphasized that the present calculation is only qualitative and thus a high level calculation including contribution of  $\pi$  to  $\sigma^*$  and  $n$  to  $\pi^*$  transitions in photocyclization reaction is desired in order to discuss the relative rate in a quantitative way.

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## The Effect of Polarizability on Reactivity of 4-Nitrophenyl Benzoate and Its Sulfur Containing Analogues with Anionic Nucleophiles in Ethanol

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2nd-order rate constants have been measured spectrophotometrically for the reactions of 4-nitrophenyl benzoate (1), S-4-nitrophenyl thiobenzoate (2) and 4-nitrophenyl thionbenzoate (3) with alkoxides, aryloxides and thioaryloxides in absolute ethanol at  $25.0 \pm 0.1$  °C. The substitution of O by polarizable S in the leaving group has little affected the reactivity of 2 toward the charge localized species (e.g.  $\text{EtO}^-$  and  $\text{CF}_3\text{CH}_2\text{O}^-$ ), while the effect of the similar replacement in the carbonyl group has led to a decrease in reactivity by a factor of 10. However, the reactivity of these esters toward charge delocalized aryloxides has been found to be in the order  $1 < 3 \leq 2$ . The effect of replaced sulfur atom on reactivity becomes more significant for the reaction with polarizable thioaryloxides, i.e. the reactivity increases in the order  $1 < 2 \ll 3$ . The difference in reactivity for the present system is attributed to a polarizability effect.

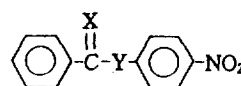
### Introduction

Nucleophilic reactivity has been suggested to be governed by many factors, such as basicity of nucleophiles and leaving groups,<sup>1</sup> ionization potential of nucleophiles,<sup>2</sup> solvation,<sup>3</sup> etc.<sup>4</sup> However, unusual reactivity has often been reported for reactions involving polarizable reactants.<sup>5</sup> Pearson has attempted to explain the unusual reactivity shown by polarizable reactants in terms of hard and soft acids and bases (HSAB) principle.<sup>5</sup> The explanations based on the HSAB principle have been satisfactory for many types of reactions in a qualitative manner. However, exceptions have frequently been reported and these could be attributed to a lack of systematic study.

We have chosen the following reaction system in order to study the effect of polarizability on reaction rates systematically. The structure of 1 would not be changed upon the substitution of the oxygen atom by a sulfur atom either in the ether-like oxygen (1→2) or in the carbonyl oxygen (1→3). However, the polarizability of the reaction center would

be considered to increase gradually but significantly. Besides, the nucleophiles employed in the present study are in a wide range of polarizability, such as charge localized alkoxides ( $\text{EtO}^-$  and  $\text{CF}_3\text{CH}_2\text{O}^-$ ), charge delocalized aryloxides and an oximate ( $\text{Ox}^-$ ), and charge delocalized polarizable thioaryloxides ( $\text{PhS}^-$  and  $p\text{-ClPhS}^-$ ). Thus, the present study would give us an important information regarding polarizability effect on reaction rates.

Since the acylated coenzyme A, an intermediate in many biological reactions, was known to be a thiol ester, studies of thiol esters have been accelerated.<sup>6</sup> However thion esters have not intensively been studied due to difficulties in preparations. The substrates studied in the present investigation are biologically important. Therefore, the present study would be considered to help us understand the reactivity of the biologically important compounds.



- 1 : X=Y=O, 4-nitrophenyl benzoate  
 2 : X=O, Y=S, S-4-nitrophenyl thiobenzoate  
 3 : X=S, Y=O, 4-nitrophenyl thionbenzoate