

## Imidoyl Halide 의 가수분해 반응메카니즘과 그의 반응속도론적 연구

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### Kinetics and Mechanism of the Hydrolysis of Imidoyl Halides

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**요 약.** *N*-(2,4-dinitrophenyl)-benzimidoyl chloride 의 여러가지 유도체의 가수분해 속도상수를 측정하여 넓은 pH 범위에서 잘 맞는 반응속도식을 구하였다. 이 식에 의하면 아직 잘 알려져 있지 않은 산성과 염기성 용액속에서 가수분해 반응메카니즘을 정량적으로 잘 설명할 수 있었다. 즉 pH 7.0 이하에서는 carbonium ion 중간체를 거쳐 반응이 진행되는  $S_N1$  반응과정이며, pH 8.5 이상에서는 hydroxide ion 과 imidoyl chloride 농도에 비례하는  $S_N2$  반응메카니즘이 의해 가수분해가 진행되며, pH 7.0~8.5 사이에서는 이 두 반응이 경쟁적으로 일어남을 알았다.

**ABSTRACT.** The rate constants of the derivatives of *N*-(2,4-dinitrophenyl)-benzimidoyl chloride were determined at various pH and a rate equation which can be applied over wide pH range was obtained. The reaction mechanism of hydrolysis of *N*-(2,4-dinitrophenyl)-benzimidoyl chloride which has not been studied carefully earlier in acidic and basic solution can be fully explained by the rate equation obtained. The rate equation reveals that, below pH 7.00, the hydrolysis of benzimidoyl chloride proceeds through  $S_N2$  reaction to form a carbonium ion intermediate. Above pH 8.5, however, the hydrolysis proceeds through the  $S_N1$  type reaction which depends on hydroxide ion and imidoyl chloride concentration. At pH 7.0~8.5, two reactions occur competitively.

#### INTRODUCTION

The kinetic studies of the substitution and hydrolysis reaction of azomethines such as carbon-nitrogen double bonds has been extensively studied. The most characteristic reaction of the imidoyl chlorides, and one in which they show

many similarities to the acyl chlorides, is substitution of halogen by a nucleophile and its applications to organic synthesis<sup>1-4</sup> especially to heterocyclic compound synthesis has been reported<sup>5</sup>. Moreover, in the organic reactions the intermediacy of an imidoyl halide has been proved. For example, in Stephan aldehyde

synthesis<sup>6</sup>, Beckmann rearrangement<sup>7</sup> and von Broun degradation<sup>8</sup> etc. In spite of its many applications to organic synthesis the mechanism of substitution of halide of the imidoyl chloride less well understood and has been the subject of only a few kinetic studies<sup>9,10</sup>.

The kinetic of hydrolysis of several derivatives of imidoyl chlorides has been studied in aqueous acetone by Ugi, Beck and Fetzer<sup>10</sup>. They have suggested a two-step mechanism involving a nitrilium ion pair intermediate. However these studies were carried out only in neutral media and for a limited number of compounds. In this paper, we wish to reveal the mechanism of hydrolysis of *N*-(2,4-dinitrophenyl)-benzimidoyl chlorides based on the substituent, solvent and salt effect on the rate constant and its change with pH.

### EXPERIMENTAL

Benzoyl chloride (17.5 ml) and 2,4-dinitroaniline (23 g) were boiled in pyridine solvent (25 ml). The product of hydrolysis, amide (1 mole) was prepared by refluxing for 5 hours with phosphorus pentachloride (1 mole) in dry benzene. After removing benzene and phosphoryl chloride by vacuum distillations bright yellow powder of *N*-(2,4-dinitrophenyl)-benzimidoyl chloride was obtained m. p 122°C (lit: 121~122°C)<sup>11</sup>. Other derivatives of benzimidoyl chloride (*p*-Cl, *p*-NO<sub>2</sub> & *m*-NO<sub>2</sub>) were also prepared as previously described. The melting point and maximum wave length ( $\lambda_{max}$ ) of benzimidoyl chloride derivatives are shown in Table 1.

Reagents used and all buffer solutions were prepared from reagent grade chemicals (Merk). The pH of buffer solutions were determined by Zerometric II pH meter (Beckman) and the ionic strength was kept constant at 0.1 by adding sodium chloride solution except for pH 1. The rate vessels used were 100 ml. volumetric flasks

and kinetic runs were made in water at 25°C.

At zero time, 0.4 ml. of a freshly prepared chloroform solution ( $5 \times 10^{-3} M$ ) of *N*-(2,4-dinitrophenyl)-benzimidoyl chloride (NBI) was pipetted into the 100 ml. flask containing 99~99.6 ml. of buffer solution. The sample were analyzed on Beckman model DU spectrometer at 252 nm. The product of hydrolysis, amide was

Table 1. The melting point and maximum wave length of imidoyl chloride derivatives

imidoyl chloride	m. p (°C)	$\lambda_{max}$ (nm)
$C_6H_5C(Cl)=N-C_6H_3(NO_2)_2$ -(2,4)	121~122	252
$4-NO_2-C_6H_4-C(Cl)=N-C_6H_3(NO_2)_2$ -(2,4)	165~167	283
$4-Cl-C_6H_4-C(Cl)=N-C_6H_3(NO_2)_2$ -(2,4)	188~190	276
$3-NO_2-C_6H_4-C(Cl)=N-C_6H_3(NO_2)_2$ -(2,4)	155~157	245
$*C_6H_5-C(=O)-NH-C_6H_3(NO_2)_2$ (2,4)	200~201	
$*4-NO_2-C_6H_4-C(=O)-NH-C_6H_3(NO_2)_2$ (2,4)	195~196	
$*4-Cl-C_6H_4-C(=O)-NH-C_6H_3(NO_2)_2$ (2,4)	195	
$*3-NO_2-C_6H_4-C(=O)-NH-C_6H_3(NO_2)_2$ (2,4)	158~159	

\*Hydrolysis products of benzimidoyl chlorides

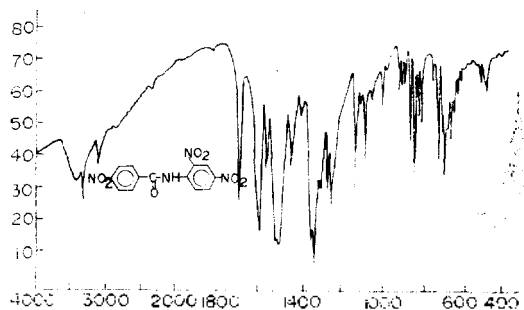


Fig. 1. IR spectrum of *N*-(2,4-dinitrophenyl)-*p*-nitrobenzamide.

identified by the melting point (150~9°C) and IR spectrum (Fig. 1).

## RESULTS

**Determination of Rate Constant of Hydrolysis of Benzimidoyl Chloride.** The initial concentration of NBI ( $2 \times 10^{-5} M$ ) was kept constant over wide pH range. Table 2 gives an example of the change of optical density of NBI with time at 252 nm and pH 4.5 and Fig. 2 shows a logarithmic plots of optical density (OD) vs. time at constant pH. Under these conditions, the reactions followed first-order kinetics. The first-order rate constants ( $k_t$ ) calculated from the slope at various pH are given in Table 3 and Fig. 3 shows pH-rate profile of this reac-

tion. Rate constants of the other derivatives of benzimidoyl chloride were determined by the same way.

**Salt Effect.** The salt effect on the rates of hydrolysis of benzimidoyl chloride was observed with changing the concentration of chloride ion at pH 4.75. As shown in Table 4, the value of rate constant was decreased as the concentration of chloride ion increased.

**Solvent Effect.** To examine the effect of ionizing power of solvent the rate of hydrolysis of benzimidoyl chloride was studied in various methanol-water mixture. The results at pH 4.75 and 10.5 are summarized in Table 5.

Table 2. The change of optical density (OD) of *N*-(2,4-dinitrophenyl)-benzimidoyl chloride (NBI) with time of pH 4.50 & 25°C

NBI = $2.0 \times 10^{-5} M$	
Time (sec.) $\times 10^{-2}$	OD
1.20	0.418
2.00	0.405
3.50	0.387
4.80	0.372
7.20	0.345
8.50	0.333
9.90	0.313

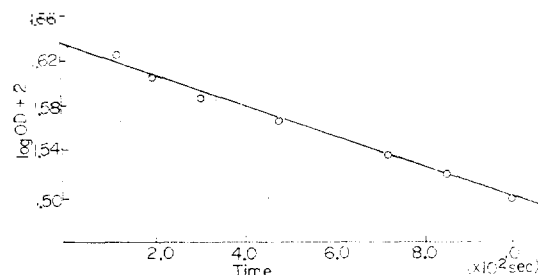


Fig. 2. The plots of  $\log(N-(2,4\text{-dinitrophenyl})\text{-benzimidoyl chloride})$  vs. time at pH 4.50 and 25°C

Table 3. The rate constants for the hydrolysis of *N*-(2,4-dinitrophenyl)-benzimidoyl chloride at various pH & 25°C and 0.1 ionic strength.

Buffer solution	pH	$k_{\text{obs}} (\text{sec}^{-1})$	$k_{\text{calc}} (\text{sec}^{-1})^*$
HCl	0.5	$8.375 \times 10^{-6}$	$1.949 \times 10^{-5}$
	1.0	$1.336 \times 10^{-5}$	$1.949 \times 10^{-5}$
	1.5	$1.645 \times 10^{-5}$	$1.949 \times 10^{-5}$
	2.0	$1.474 \times 10^{-5}$	$1.949 \times 10^{-5}$
	2.5	$2.086 \times 10^{-5}$	$1.949 \times 10^{-5}$
	3.0	$2.047 \times 10^{-5}$	$1.949 \times 10^{-5}$
HAc + NaAc	3.5	$1.506 \times 10^{-5}$	$1.949 \times 10^{-5}$
	4.0	$1.727 \times 10^{-5}$	$1.949 \times 10^{-5}$
	4.5	$1.675 \times 10^{-5}$	$1.949 \times 10^{-5}$
	5.0	$2.201 \times 10^{-5}$	$1.949 \times 10^{-5}$
	5.5	$1.610 \times 10^{-5}$	$1.949 \times 10^{-5}$
	6.0	$1.978 \times 10^{-5}$	$1.949 \times 10^{-5}$
KH <sub>2</sub> PO <sub>4</sub> + K <sub>2</sub> HPO <sub>4</sub>	7.0	$1.949 \times 10^{-5}$	$1.949 \times 10^{-5}$
	7.5	$1.980 \times 10^{-5}$	$2.129 \times 10^{-5}$
H <sub>3</sub> BO <sub>3</sub> + NaOH	8.0	$2.870 \times 10^{-5}$	$2.549 \times 10^{-5}$
	8.5	$5.198 \times 10^{-5}$	$3.846 \times 10^{-5}$
	9.0	$1.059 \times 10^{-4}$	$7.953 \times 10^{-4}$
	9.5	$3.140 \times 10^{-4}$	$2.092 \times 10^{-4}$
	10.0	$6.028 \times 10^{-4}$	$6.199 \times 10^{-4}$
	10.5	$1.920 \times 10^{-3}$	$1.829 \times 10^{-3}$
NaOH	11.0	$1.560 \times 10^{-3}$	$6.023 \times 10^{-3}$
	11.5	$2.339 \times 10^{-3}$	$1.800 \times 10^{-2}$

\*The value is calculated according to the equation (2).

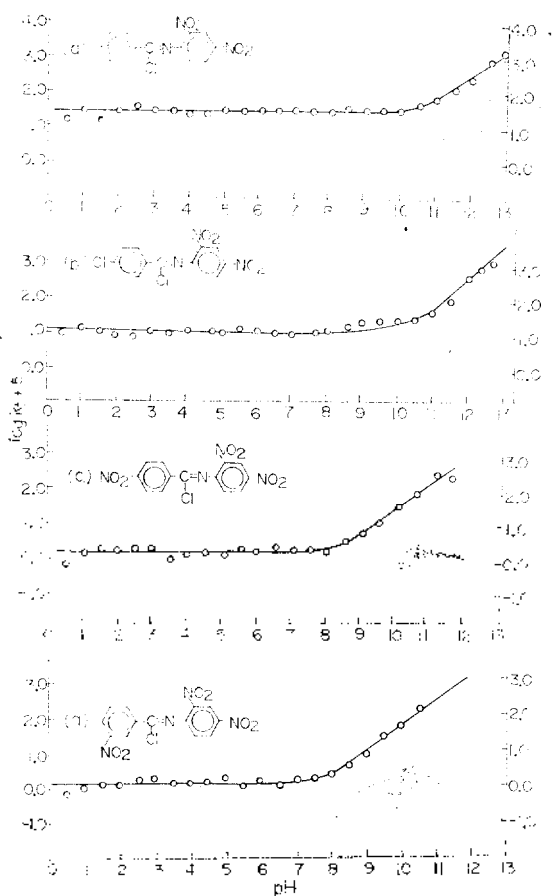


Fig. 3. pH-rate profile for the hydrolysis of *N*-(2,4-dinitrophenyl)-benzimidoyl chloride at 25°C. The points are experimental; The solid line is the theoretical curve

Table 4. The change of rate constants for the hydrolysis of *N*-(2,4-dinitrophenyl)-benzimidoyl chloride with the concentration of sodium chloride at pH 4.75.

pH	$k_{\text{obs}}(\text{sec}^{-1})$	NaCl(mole $l^{-1}$ )
4.75	$7.59 \times 10^{-4}$	0.01
4.75	$6.85 \times 10^{-4}$	0.03
4.75	$5.37 \times 10^{-4}$	0.05
4.75	$4.77 \times 10^{-4}$	0.07
4.75	$3.84 \times 10^{-4}$	0.09

**Substitution Effect.** Fig. 4 and 5 show the plot of  $\log k$  for the hydrolysis of substituted

Table 5. The rate constants for the hydrolysis of *N*-(2,4-dinitrophenyl)-*p*-chloro-benzimidoyl chloride in aqueous metanol at pH 4.75 and 10.5 & 25°C.

Water (vol %)	Rate constants( $\text{sec}^{-1}$ )	
	pH 4.75	pH 10.5
10	$3.205 \times 10^{-6}$	$4.803 \times 10^{-4}$
20	$1.380 \times 10^{-5}$	$3.659 \times 10^{-4}$
30	$1.790 \times 10^{-5}$	$8.210 \times 10^{-5}$
40	$2.990 \times 10^{-5}$	$8.350 \times 10^{-5}$
50	$4.040 \times 10^{-5}$	$6.250 \times 10^{-5}$

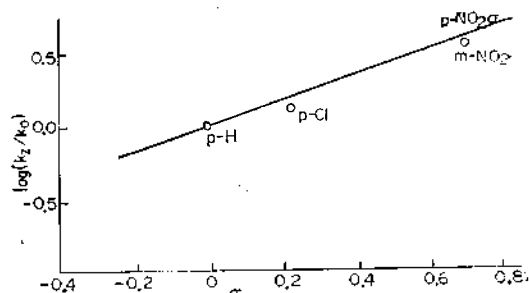


Fig. 4. Hammett plot for the hydrolysis of NBL derivatives in 60% metanol at pH 4.75

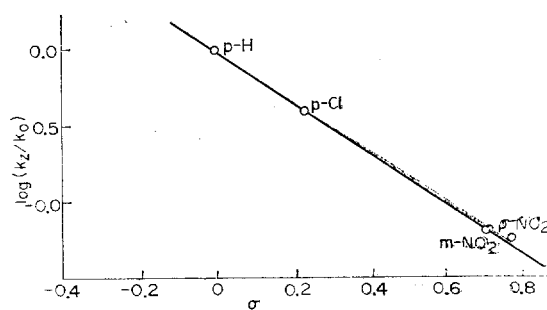


Fig. 5. Hammett plot for the hydrolysis of NBL derivatives in 60% metanol at pH 11.

benzimidoyl chloride (*p*-H, *p*-Cl, *p*-NO<sub>2</sub> and *m*-NO<sub>2</sub>). As shown in Fig. 4 and 5, at low pH, electron-donating substituent speed up ( $\rho = -1.69$ ) and at high pH, slow the rate of hydrolysis ( $\rho = 0.89$ ) These results suggested that the hydrolysis proceeds through different mechanisms in acidic and basic media.

## DISCUSSION

**Determination of the Rate Equation for the Hydrolysis of NBI.** Analysis of Fig. 3 shows that the total rate constant ( $k_{obs}$ ) is given by an expression of the form.

$$\begin{aligned} \text{Rate} &= -\frac{d[\text{NBI}]}{dt} = k_{obs}[\text{NBI}] \\ &= \{k_0 + k_{OH}[\text{OH}^-]\} [\text{NBI}] \\ \therefore k_{obs} &= k_0 + k_{OH}[\text{OH}^-] \quad (1) \end{aligned}$$

where  $k_0$  is the pH independent part i.e, it is the rate constant due to catalysis of  $\text{H}_2\text{O}$  and the second term is pH dependent part.  $k_0$  and  $k_{OH}$  for the hydrolysis of *N*-(2,4-dinitrophenyl)-benzimidoyl chloride can be calculated as followings:  $k_{OH} = 2.87 \times 10^{-1} \text{sec.}^{-1}$  is obtained from the values of the rate constant at pH 11.00 and pH 12.50 and the rate constant at low pH is taken as the  $k_0 = 3.10 \times 10^{-4} \text{sec.}^{-1}$ .

Substituting these values into the equation(1).

$$k_{obs} = 3.10 \times 10^{-4} + 2.87 \times 10^{-1}[\text{OH}^-] \quad (2)$$

Fig. 3 and Table 3 show that the values of over all rate constant,  $k_{obs}$  calculated by equation (2) are in good agreement with the observed values. Similarly, the rate equations obtained for the derivatives of the benzimidoyl chloride are as follows:

*N*-(2,4-dinitrophenyl)-benzimidoyl chloride:

$$k_{obs} = 3.10 \times 10^{-4} + 2.87 \times 10^{-1}[\text{OH}^-]$$

*N*-(2,4-dinitrophenyl)-*p*-chlorobenzimidoyl chloride:

$$k_{obs} = 7.08 \times 10^{-4} + 5.08 \times 10^{-1}[\text{OH}^-]$$

*N*-(2,4-dinitrophenyl)-*m*-nitrobenzimidoyl chloride:

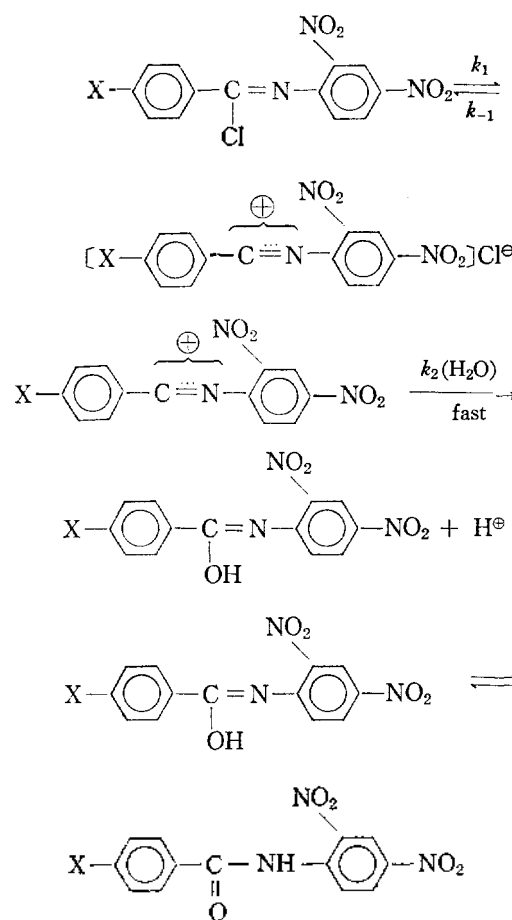
$$k_{obs} = 1.949 \times 10^{-5} + 6.004[\text{OH}^-]$$

*N*-(2,4-dinitrophenyl)-*p*-nitrobenzimidoyl chloride:

$$k_{obs} = 1.995 \times 10^{-5} + 3.041[\text{OH}^-]$$

**Mechanism of Hydrolysis of Benzimidoyl Chloride.** At low pH, as shown in Fig. 3, the rate constant remains constant. From the effect of solvent, salt, substituent and the rate law, the following  $S_N1$  reaction mechanism is proposed in this pH range;

Scheme 1.



At the second step, water molecule combines with carbonium ion to gives an unstable enol. This unstable enol form converts to stable keto form rapidly. In this mechanism, the first will be the rate determining step. The solvent effect in Table 5 also supports above  $S_N1$  mechanism. In low range of pH, the rate of hydrolysis facilitate with the increase of water content since at the rate determining step, a separation

of charge occurred. As shown by the Hammett plots of Fig. 4, at low pH, it is found that the rate is accelerated by an electron donating group with  $\rho = -1.69$ . These results are interpreted in terms of stabilization of carbonium ion and acceleration of the leaving of chloride ion by the electron-donating group.

As shown in Table 4, the rate of reaction decreases as the concentration of chloride ion increases. This mass law effect is also explained by the following general rate equation for the reversible  $S_N1$  reaction.

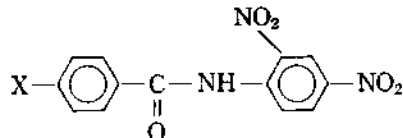
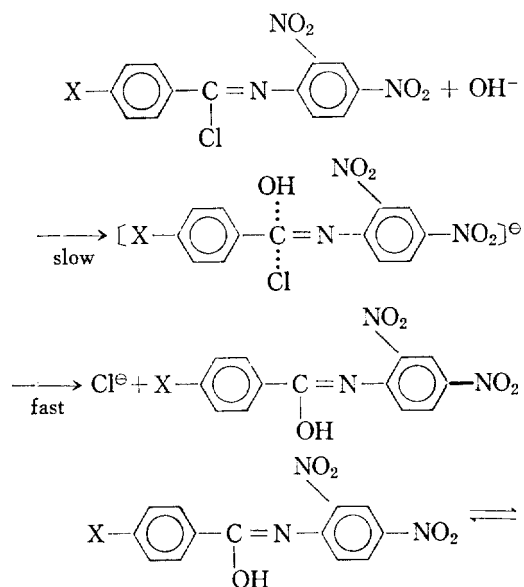
$$\text{Rate} = \frac{k_1 k_2 [\text{NBI}] [\text{H}_2\text{O}]}{k_1 [\text{Cl}^-] + k_2 [\text{H}_2\text{O}]} = \frac{k_1 k_2' [\text{NBI}]}{k_1 [\text{Cl}^-] + k_2'} \quad (3)$$

if the chloride ion concentration is constant, the rate equation becomes

$$\text{Rate} = k_0 [\text{NBI}]$$

As shown in Fig. 3 at high pH, the rate of hydrolysis of imidoyl chloride is proportional to the hydroxide ion concentration. From this rate law and other facts, a following  $S_N2$  mechanism is proposed.

Scheme 2.



This mechanism is also supported by the solvent effect. i.e., in general,  $S_N2$  in which neutral molecule and an anion form an ion pair at transition state is favored in nonpolar solvent.

As would be expected from  $S_N2$  mechanism, the attacking of hydroxide ion to imidoyl chloride is accelerated by the electron withdrawing group as shown in Fig. 5 ( $\rho = 0.89$ )

Moreover, from the positive value of  $\rho$ , it can be concluded that the bond formation is more important than the bond breaking at the transition state. If the bond breaking is the rate determination step, the value is rather small than zero since the reaction becomes faster as the electron density increases. At pH 7.0~8.5, from the rate equation, it can be concluded that the  $S_N1$  and  $S_N2$  reaction occurs competitively.

## CONCLUSION

In this paper, the kinetics and mechanism of hydrolysis of the derivatives of *N*-(2,4-dinitrophenyl)-benzimidoyl chlorides over a wide pH range were presented and analyzed in detail.

(1) A general rate equation which can be applied over wide pH was obtained:

$$k_{\text{obs}} = k_0 + k_{\text{OH}}[\text{OH}^-]$$

where the  $k_0$  is the pH independent part and the second term is dependent upon only hydroxide ion. The rate equations of the derivative of the benzimidoyl chloride are followings;

*N*-(2,4-dinitrophenyl)-benzimidoyl chloride;

$$k_{\text{obs}} = 3.10 \times 10^{-4} + 2.81 \times 10^{-1}[\text{OH}^-]$$

*N*-(2,4-dinitrophenyl)-*p*-chlorobenzimidoyl chloride;

$$k_{\text{obs}} = 7.08 \times 10^{-4} + 5.08 \times 10^{-1}[\text{OH}^-]$$

*N*-(2,4-dinitrobenzimidoyl chloride;

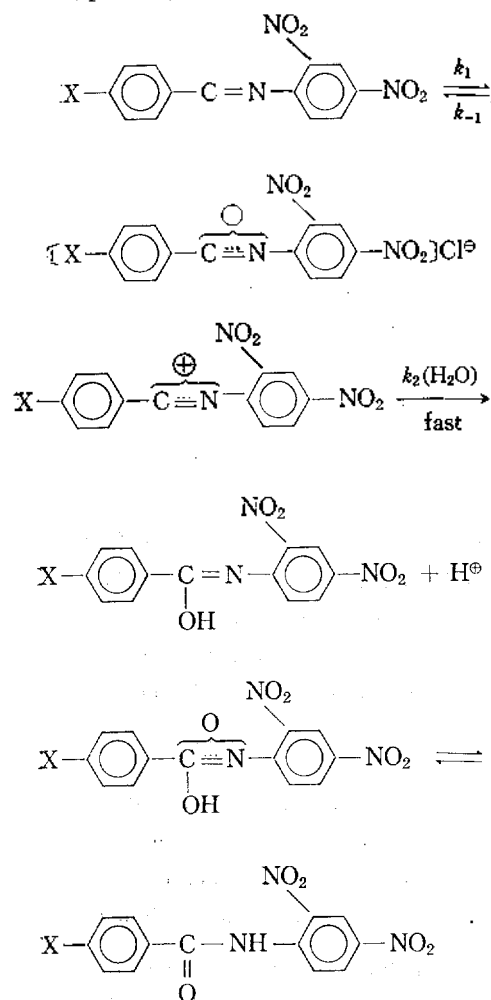
$$k_{\text{obs}} = 1.949 \times 10^{-5} + 6.004 [\text{OH}^-]$$

*N*-(2,4-dinitrophenyl)-*p*-nitrobenzimidoyl chloride;

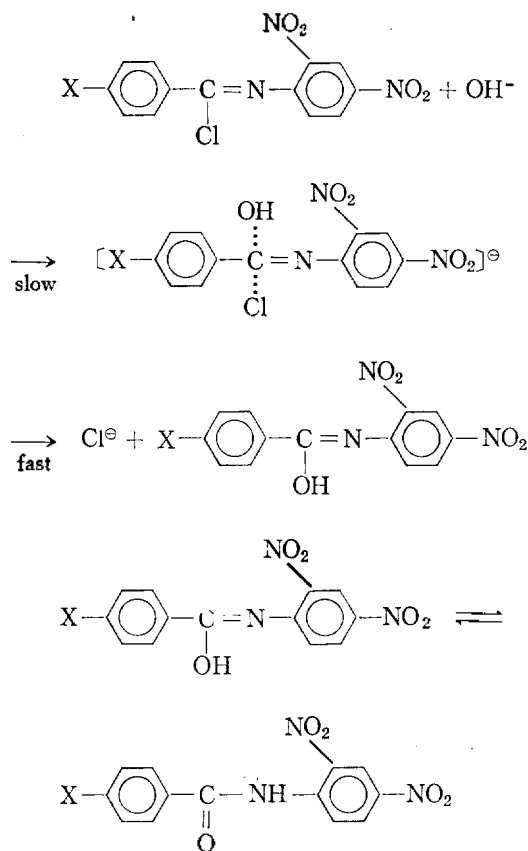
$$k_{\text{obs}} = 1.995 \times 10^{-5} + 3.041 [\text{OH}^-]$$

(2) From the effect of salt, solvent, substitution and rate law, the following  $S_N1$  and  $S_N2$  reaction mechanism for the hydrolysis of imidoyl chloride are proposed;

Below pH 7.0,



Above pH 8.5,



and at pH 7.0~8.5 the  $S_N1$  and  $S_N2$  reaction occurs competitively.

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