

Nickel-Phthalocyanine 생성의 반응속도론적 연구

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Kinetics of the Formation of Nickel-Phthalocyanine

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Abstract: A mechanism for the ring formation of nickel phthalocyanine (Ni-Pc) has been proposed based on chemical kinetics. The effect of the catalyst on the rate was examined, and ammonium molybdate has been found to be the most effective. The reaction order of the ring formation was determined to be of the 1st order over all, with only the concentration of urea affecting the rate of the ring formation. All the results including thermodynamic parameters support a conclusion that the rate-determining step seems to be the enolization of the urea-catalyst transition complex, followed by fast decomposition of the tautomeric enolized urea into ammonia and isocyanic acid. These intermediates then reacted with the phthalic anhydride to form imino and diimino-phthalimide, which condense to form nickel phthalocyanine in the presence of the nickel cation.

Introduction

In 1907, Braun and Tcherniac obtained a blue substance by heating o-cyanobenzamide.¹ Twenty years later, an attempt to synthesize dinitrile by heating o-dibromobenzene in pyridine was undertaken. Instead of the desired dinitrile, a similar unknown blue substance was obtained which is now known as phthalocyanine. Since then, extensive studies of the physical and chemical aspects of phthalocyanine and its metallic complexes have been undertaken by a number of research groups. For synthesis of this compound, there are three common

methods; the phthalonitrile process,² Wyler's method³⁻⁵ and a reaction of o-cyanobenzamide with metal⁶ are the typical synthetic routes to phthalocyanine. Yet, oddly enough, none of the methods have been investigated kinetically to determine the ring formation mechanism of phthalocyanine.

In this study, therefore, the ring formation mechanism of metallic phthalocyanine, particularly nickel-coordinated, has been examined by chemical kinetics. Wyler's method³⁻⁵ was adopted in this investigation for the synthesis using phthalic anhydride and urea as the main starting materials.

Results and Discussion

Kinetics. It is known, in general, that certain suitable catalysts accelerate the rate of ring formation of phthalocyanine (Pc) and its metallic complexes, and the common ones for the purpose are ferric chloride, aluminum chloride, titanium tetrachloride and ammonium molybdate. The effectiveness of these catalysts for the formation of nickel-phthalocyanine (Ni-Pc) has investigated here by the kinetic method.

The rate of Ni-Pc formation using 0.05 mole of phthalic anhydride and 0.25 mole of urea at 160°C and 0.25 mole of urea at 160°C and 180°C are tabulated in Table 1. And also, in order to compare the effectiveness of the various catalysts used, the rate constants determined by the same method are summarized in Table

2. It should be noted that the amount of titanium tetrachloride and ammonium molybdate used was one tenth as much as the others.

It can readily be seen from Table 2 that ammonium molybdate is the most effective as the reaction is twice as fast as the reaction using equimolar titanium chloride. Thus, ammonium molybdate was used exclusively in the following kinetic runs.

Next, the variation of optical density measured at definite intervals during Ni-Pc formation from phthalic anhydride, urea and nickel chloride as starting and ammonium molybdate as a catalyst was substituted into the equation $\log (D_{\infty}-D_0)/(D_{\infty}-D_t)$. The absorption maximum was at 440 nm. Rate constants thus obtained are presented in Table 3 and the data plotted in Fig. 1.

Table 1. Rate constants of Ni-Pc using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.015 M) as catalyst.

Time (min)	At 160°C OD at 440 nm	<i>k</i>
540	0.182	7.64×10^{-6} (sec ⁻¹)
600	0.192	7.29
660	0.236	7.74
720	0.256	7.88
∞	0.830	$x = 7.64 \pm 0.30$
	At 180°C	
150	0.236	4.10×10^{-6} (sec ⁻¹)
180	0.256	4.64
210	0.387	4.98
∞	0.830	$x = 4.57 \pm 0.66$

Table 2. The effect of catalysts on the rate of Ni-Pc formation

Catalysts	<i>k</i> (sec ⁻¹) at 160°C	<i>k</i> (sec ⁻¹) at 180°C
$\text{AlCl}_3 - \text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	$(5.69 \pm 0.58) \cdot 10^{-6}$	$(3.50 \pm 0.85) \cdot 10^{-4}$
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	$(7.64 \pm 0.39) \cdot 10^{-6}$	$(4.57 \pm 0.66) \cdot 10^{-5}$
TiCl_3	$(1.29 \pm 0.14) \cdot 10^{-5}$	$(3.81 \pm 0.66) \cdot 10^{-5}$
$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}^*$	$(2.68 \pm 0.15) \cdot 10^{-5}$	

*0.0015 M, one tenth of the amount of the other two.

Table 3. Rate constants of Ni-Pc formation in 10^{-4} M 95% H_2SO_4 solution at 150°C

Time(min)	OD at 440 nm	$2.303 \log \frac{D_{\infty} - D_0}{D_{\infty} - D_t}$	$k \times 10^6 \text{ (sec}^{-1}\text{)}$
1,260	0.132	0.1700	2.25
1,320	0.138	0.1783	2.25
1,380	0.143	0.1856	2.24
1,440	0.154	0.2013	2.33
1,500	0.169	0.2232	2.48
1,560	0.183	0.2432	2.60
∞	0.845		$x = 2.36 \pm 0.15$

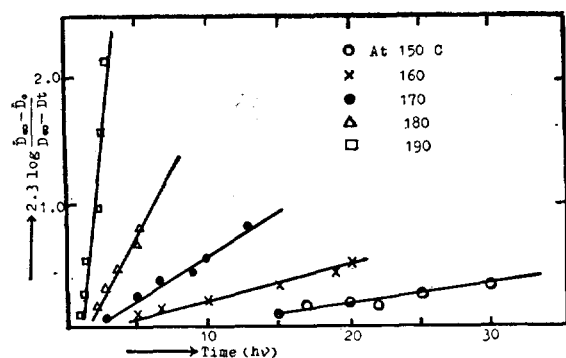


Fig. 1. The 1st order plot for the formation of Ni-Pc.

The data in Table 3 and Fig. 1 show that the reaction is apparently 1st order. However, it has been uncertain which of the components

in the reaction mixture determine the reaction order. Therefore, the concentration of each of the components was varied to determine their effect on the reaction order. First of all, the concentration of phthalic anhydride, which is supposed to be one of the major contributing component for the Ni-Pc formation, was changed and the reaction rate measured using the described above. The results of the measurement are shown in Table 4 and the data displayed in Fig. 2. In the same way, the rates were measured varying the concentration of urea. These results are summarized in Table 5 and presented in Fig. 3 and 4.

Table 4. Rate constants measured for different concentrations of phthalic anhydride.*

Molar concentration	T(min)	OD(430 nm)	$k \times 10^6 \text{ (sec}^{-1}\text{)}$
PA = 1×10^{-4}	15	0.027	2.81
Urea = 4×10^{-4}	30	0.042	2.20
NiCl_2 = 2.5×10^{-5}	45	0.072	2.56
Am. Mo. = 2.5×10^{-6}	60	0.102	2.75
	75	0.120	2.62
	90	0.143	2.63
	120	0.158	2.16
	150	0.123	2.44
	∞	1.08	Aver. 2.52 ± 0.24

PA	$= 3 \times 10^{-4}$	10	0.017	2.64
Urea	$= 4 \times 10^{-4}$	20	0.030	2.33
NiCl ₂	$= 2.5 \times 10^{-5}$	30	0.039	2.04
Am. Mo.	$= 2.5 \times 10^{-4}$	60	0.098	2.13
		80	0.138	2.71
		100	0.164	2.74
		∞	1.08	Aver. 2.43×0.31

* The temperature was kept at 150°C in both cases.

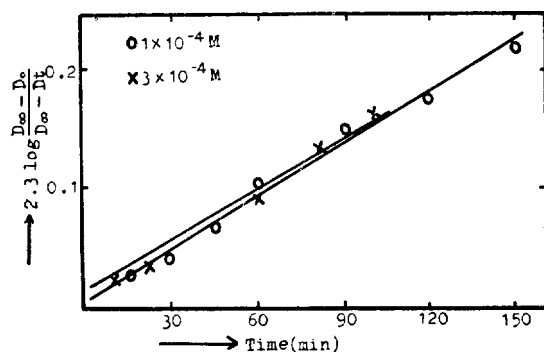


Fig. 2. The effect of phthalic anhydride concentration on the reaction rate for Ni-Pc.

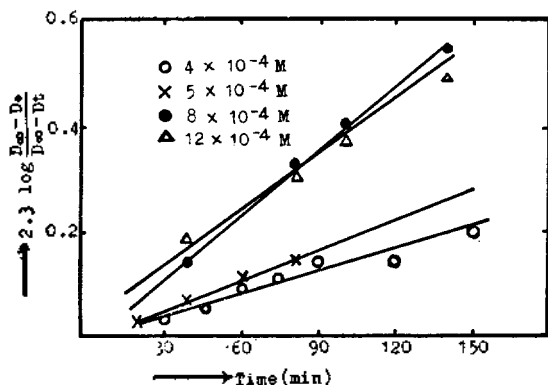


Fig. 3. Dependence of reaction rate of the Ni-Pc formation on concentration of urea (at 150°C).

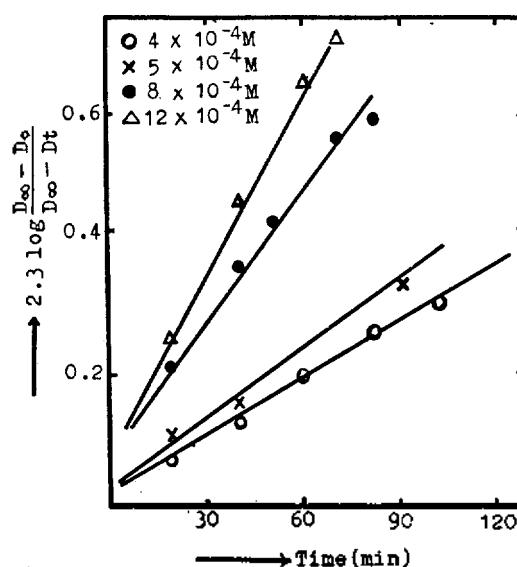


Fig. 4. Dependence of reaction rate of the Ni-Pc formation on varying concentration of urea (at 160°C).

Table 5. The effect of urea concentration on rate constants for the Ni-Pc formation.

$M \times 10^4$	Rate constants $\times 10^6 \text{ sec}^{-1}$	
	at 150°C	at 160°C
4	2.52 ± 0.24	5.79 ± 0.16
5	3.30 ± 0.31	7.21 ± 0.38
8	7.76 ± 0.24	17.2 ± 1.20
12	7.56 ± 0.33	23.4 ± 1.20

From the *Tables* and the *Figures* shown above, it can be seen that the rate constants changed insignificantly with change of concentration, phthalic anhydride. That is, in spite of the fact that the concentration of phthalic anhydride in one kinetic run was three times that in the

other run, the rate constants were $2.52 \times 10^{-5} \text{ sec}^{-1}$ and $2.43 \times 10^{-5} \text{ sec}^{-1}$ respectively.

These are not significantly different from each other compared to the difference in concentration. Thus, it is obvious that the

Table 6. Dependence of rate constants of the Ni-Pc formation on the concentration of nickel chloride and ammonium molybdate.

Reactants	$M \times 10^4$	$k \times 10^5 \text{ sec}^{-1}$	
		at 150°C	at 160°C
NiCl ₂	2	2.53 ± 0.14	5.86 ± 0.17
	4	2.62 ± 0.08	5.85 ± 0.14
	2	2.62 ± 0.20	5.72 ± 0.17
(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	4	2.51 ± 0.11	5.73 ± 0.05

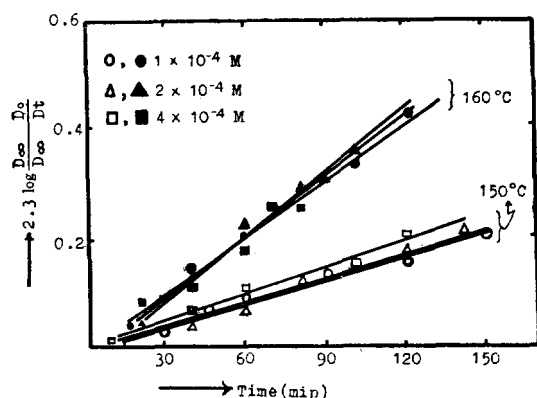


Fig. 5. The rate constant of Ni-Pc formation for different concentrations of NiCl₂

concentration of phthalic anhydride does not affect the reaction order. On the other hand, it is from Table 5 and Fig. 3 and 4 that the rate constants changed significantly in accordance with the change in concentration of urea. At a glance, it would seem likely that the reaction rate is proportional to the concentration of urea used, except in the case of 12 mole at 150°C. This is shown in Fig. 5, in which a linear relationship between the rate constants and the concentration of urea exists. This means unequivocally that the reaction rate of Ni-Pc formation is proportional to the first power of the concentration of urea. However, since not only phthalic anhydride and urea but also nickel chloride and ammonium molybdate participated as catalysts in the reaction, the dependence of the

reaction rate on these was also examined in the same way in order to confirm the conclusion mentioned above. The results thus obtained are summarized in Table 6 and plotted in Figs. 5 and 6.

It can be seen from Table 6 that all the rate constants at the same temperature are almost the same no matter what reactants and concentration were used, or at least varied only within the limits of experimental error. The average values of these rate constants at each temperature are $2.57 \times 10^{-5} \text{ sec}^{-1}$ and $5.79 \times 10^{-5} \text{ sec}^{-1}$, respectively, and these values coincide with the values at the initial condition, in which none of the concentrations were changed, $2.52 \times 10^{-5} \text{ sec}^{-1}$ and $5.79 \times 10^{-5} \text{ sec}^{-1}$ in Table 5. This means apparently that neither nickel chloride nor ammonium molybdate affects the reaction rate. The independence of the rates from the concentration are displayed in Figures 5 and 6.

In order to supplement all the data obtained above, thermodynamic parameters were also calculated⁷ from the rate constants in Table 5 and are summarized in Table 7.

Mechanism. It remains to examine the implications of these findings for the ring formation mechanism. The fact that the reaction is first order with respect to urea means that urea should participate in the rate determining step of the over-all reaction. In other words, urea performs some role in the transition state of the reaction. According to the transition

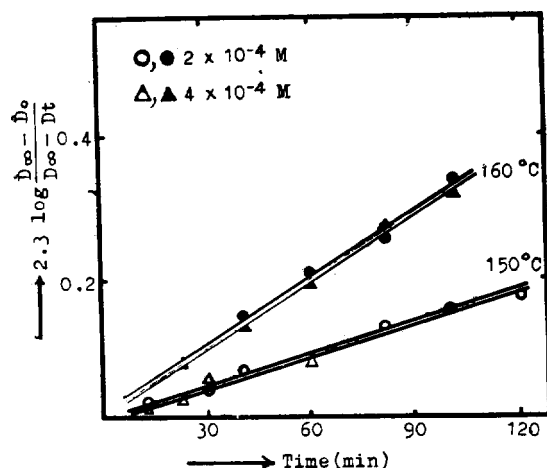
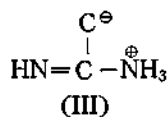
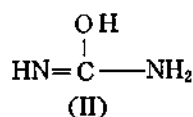
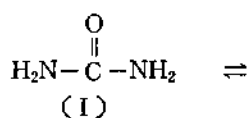


Fig. 6. The rate constant of Ni-Pc formation for different concentrations of ammonium molybdate.

Table 7. Thermodynamic parameters for the Ni-Pc formation.

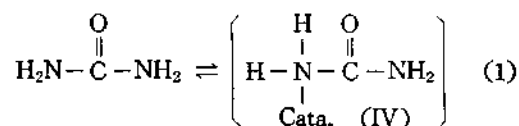
Conc. of Urea	$E_a(\text{Kcal})$	$\Delta S^{**}(\text{e. u.})$
$4 \text{ M} \times 10^4$	29.01 ± 0.15	12.17
5	25.38 ± 0.08	8.57
8	25.38 ± 0.47	12.51
12	39.89 ± 0.13	39.81

state theory, since the rate of a given reaction is determined by the decomposition of an activated complex, that is, a transition state, it seems very reasonable to turn to a study of the activated complex which is supposed to be formed by urea in the rate determining step. The urea molecule can be represented by one of the following three tautomeric forms.



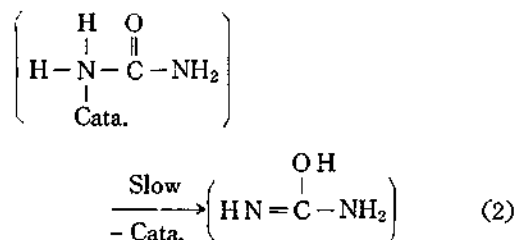
It is obvious that the keto form of (I) should be the most stable one among the three tautomers. However, one can hardly eliminate the possibility that both an enol form of (II) and a polarized form of (III) could exist as transient or intermediate phases in sort of an excited state. It is recognized that the polarized tautomeric form of (III) could be simultaneously formed due to the instability of

$\text{=}\overset{|}{\text{C}}-\text{OH}$, provided the enol form was once established. The key point in this respect is the nature of the internal driving power which operates in the 1,3-shift of the transformation of (I) into (II). Naturally, it is apparent that urea does not possess such internal driving power itself. The conversion from (I) into (II), thus, ought to be due to an external driving force. At this stage, it is adequate to recall the fact that the presence of a catalyst is required to form the Ni-Pc ring. And a reaction between the catalyst and urea rather than phthalic anhydride is to be expected because urea is the only component which affects the reaction order, not phthalic anhydride. The catalysts used for the Ni-Pc formation were aluminum chloride, ferric chloride, titanium chloride and ammonium molybdate, and all these are Lewis acids. When one of these electron deficient molecules commence to react with urea, the lone pair electrons attached to the nitrogen atoms rather than the partially positive center of the carbonyl carbon would be attached by the catalysts. Thus, the following activated complex would be formed in the reaction between urea and the catalyst.

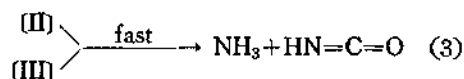


Now, it is interesting to examine the thermo-

dynamic parameters in connection with the activated complex. First of all, the positive values of the activation entropy, appearing in Table 7, for all concentrations of urea, indicate that the decomposition of the activated complex should be a first order reaction which would not be affected by any other reactants and/or solvent. A rather more important factor than the above inductive conclusion for the elucidation of the mechanism is that the activated complex must possess some internal freedom equivalent to the positive activation entropy. This would make possible the conclusion that this internal freedom causes the conversion of the tautomer (I) into (II), a conversion that could hardly take place without external driving power otherwise. Thus, the activated complex could proceed to the following decomposition in the rate-determining step.



The product in this step is apparently tautomer (II) which could further tautomerize into (III). Three tautomers should not be stable and undoubtedly decompose into ammonia and isocyanic acid as follows:

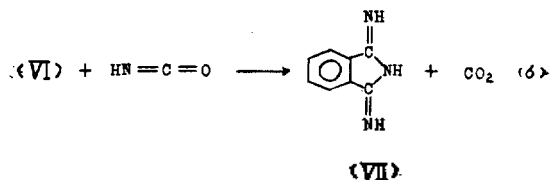
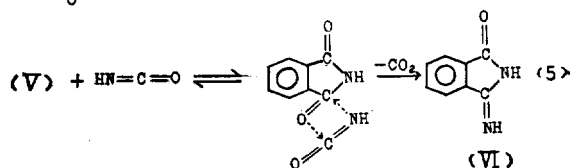
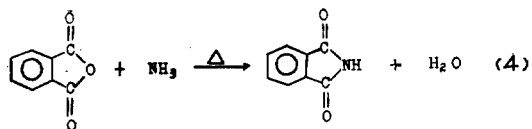


The feasibility of such a mechanism can be shown by comparison with other similar reactions. For instance, Powling and Bernstein⁸ have pointed out that all keto-enol conversions without hydration possess positive activation entropy, and the fact⁹ that the decomposition of urea produces ammonia and

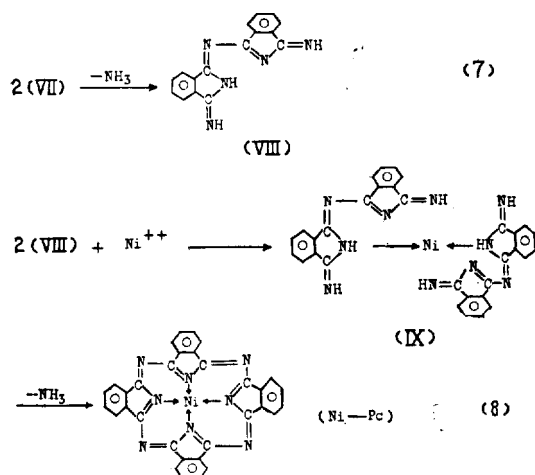
isocyanic acid also supports the above proposal of the mechanism. Ammonia, once thus obtained, reacts with the phthalic anhydride to produce phthalimide (II), product verified in this laboratory. And then, in turn, two moles of isocyanic acid should react with this phthalimide to give 1,3 diiminisindoline (VII).

The transformation of phthalimide (V) into the latter compound (VII) could presumably proceed by passing through (VI) which would be formed by a concerted four center mechanism, forming carbon dioxide. The formation of carbon dioxide in the procedure has also been verified in this laboratory. The proposed scheme of the transformation is as follows:

Two moles of compound (VII), thus produced, would chelate with each other to form intermediate (VII). The mechanism of the organic chelating has already been proposed by Linstead.¹⁰ And then, finally, two moles of the chelated intermediate would combine into nickel-phthalocyanine in the presence of nickel chloride, presumably passing through intermediates (IX). Thus, a plausible mechanistic route, which is incidentally similar with the recent pro-



posal studied by Hurley and his co-workers,¹¹ is as follows:



Experimental

Preparation of Ni-Phthalocyanine. Into 45.3g (0.25 mole) of 1, 2, 4-trichlorobenzene were added 7.5g (0.05 mole) of phthalic anhydride, 15g (0.55 mole) of urea and 1.44g (0.015 mole) of nickel chloride. The mixture was heated slowly, and at a temperature of 150°C a small amount of a mixed catalyst consisting of anhydrous aluminium chloride (0.014 mole) and ferric chloride (0.005 mole) was gradually added. The temperature of the reaction mixture was then raised and kept at 185°~190°C for 6 hrs. When cooled blue crystals formed, which were crystallized from concentrated H₂SO₄ after washing with ethanol and hot water in order to remove the solvent and inorganic compounds present. It was found that the addition of the catalyst to the reaction mixture at the initial step affects neither the rate nor the yield. Ethylene glycol, *tri-n*-butyl amine and nitrobenzene were found to be unsuitable solvents and only 1, 2, 4-trichlorobenzene was used as solvent.

Kinetic Measurements. Preliminary tests

showed that 10⁻⁴ M solutions were best suited for kinetic measurements. The calculated amounts of starting materials, including catalyst and solvent, were placed in a series of 20ml ampoules. The sealed ampoules were placed in a constant temperature bath together and individual ampoules were removed at recorded times and plunged into ice-cold water. The thermostat used regulated the temperature within 1°C. The rate of ring formation was determined by measuring the change in optical density at 430nm and 440nm, respectively. A Shimadzu Model 1 QR-50 UV spectrophotometer with glass-stopped 1cm silica cells was used for the kinetic runs.

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