

# ON THE ORGANIC SYNTHESIS RELATED TO THE SODIUM INDUSTRY

By

Haruo GOTOH

*Textile Chemical Laboratory, faculty of Textile Science  
and Technology, Shinshu University*

(Received September 10, 1962)

## CONTENTS

II On the synthesis of pentachlorophenol and the manufacture of hexachlorobenzene from Non- $\gamma$ -B. H. C.	
Introduction .....	2
Pentachlorophenol and B. H. C. ....	2
Chlorination of Benzene .....	3
Chlorination of phenol .....	7
Heat decomposition of Non- $\gamma$ -B. H. C. ....	9
Heat decomposition and simultaneous chlorination of Non- $\gamma$ -B.H.C. in the gas phase .....	10
Synthesis of pentachlorophenol with hexachlorobenzene .....	15
The illustration of the industrial process of the decomposition of Non- $\gamma$ -B.H.C. by heat and the simultaneous chlorination .....	16
Summary .....	17
References .....	18
III. Production of ethyleneimine as the raw material for the manufacture of tetramethylene-bis-NN'-ethylene urea	
Introduction .....	19
Process of the synthesis of tetramethylene-bis-ethylene urea.....	19
On the reaction among adipic dichlorododiamide, ethyleneimine and caustic soda .....	21
Manufacture of ethyleneimine .....	28
Consideration for increasing the yield of ethyleneimine .....	35
Summary .....	36
References .....	36

## II On the Synthesis of Pentachlorophenal and the Manufacture of Hexachlorobenzene from Non- $\gamma$ -B. H. C.

### INTRODUCTION

Non- $\gamma$ -B. H. C. which is the generic name of  $\alpha$ -,  $\beta$ -,  $\delta$ -,  $\epsilon$ - B. H. C. is the unavailable B. H. C. for the insecticide. This is generally given up in a corner of the workshop which manufactures B. H. C. for the sake of its no available use. The author made it utilize as a raw material for the manufacture of pentachlorophenol (P. C. P.), for he succeeded for the first time (October, 1952) to synthesize hexachlorobenzene from the Non- $\gamma$ -B. H. C. with chlorine in a gaseous phase reaction.

In view of the cheapest cost price of Non- $\gamma$ -B. H. C. which is gratis in such a workshop as producing B. H. C. for the insecticide, this process is the very economical way to manufacture pentachlorophenol. In addition, the synthetic reaction of Non- $\gamma$ -B. H. C. with chlorine is easy one from the viewpoint of heat balance in the reaction but for the fact that it is somewhat difficult to manage B. H. C. on behalf of its sublimating nature. But this difficulty will be able to be removed by means of a device of some industrial technique

### P. C. P. (PENTACHLOROPHENOL) AND B. H. C. (BENZENE HEXACHLORIDE)

**P. C. P. :** Cl content 66.5%; molecular weight 266.4, melting point 190.2°C, a white needle-shaped crystal (from benzene). When recrystallized from hydrated alcohol, it yielding  $C_6OHCl_5 \cdot H_2O$  (m. p., 174°C); boiling point 309°~310°C/754.3mm. Hg, 195°C/16mm. Hg; having sublimating property, and a weak peculiar odor; stimulating the mucous membrane hardly; hardly soluble in water; viz., 0.0005g in 100g water at 0.0018g at 27°C, 0.0035g at 50°C, 0.0058g at 62°C, 0.0085g at 70°C.

P. C. P. is stable against heat, and does not decompose on long heating at high temperature, but decomposes by a very little when heated in water or acidic aqueous solutions for a long time.

#### B. H. C.:

$\alpha$ -isomer,	m. p. 157°, 158°, 158.2°C
$\beta$ -isomer,	m. p. 297°, 310°, 312°C
$\gamma$ -isomer,	m. p. 112°~113°C
$\delta$ -isomer,	m. p. 138~139°C
$\epsilon$ -isomer,	m. p. 218.5~219.3°C

Composition of B. H. C. is as follows;

$\alpha=70\%$ ,	$\beta=5\%$ ,	$\gamma=10\ 12\%$ ,	$\delta=13\ 15\%^{1)}$
$=55\%$ ,	$=14\%$ ,	$=12\%$ ,	$=8\%^{2)}$

Isomer contents of unavailable B. H. C. after extracting the  $\gamma$ -B. H. C. are;

$$\alpha=90\%, \quad \beta=10\%, \quad \gamma=0.5\%.$$

13.2g  $\gamma$ -B. H. C. is obtained ( $\gamma$ -B. H. C. content 60~65%) from 100g B. H. C.; the yield is about 75% ( $\gamma$ -content 11g/100g B. H. C.).

**The Uses of P. C. P.** this is used as an antiseptic or a disinfectant about woods, articles made of woods, bamboo-wares, pulps, papers, woven goods, starch, dextrine, rubber, glue, casein, albumin, hides etc.

#### Material balance of $\gamma$ -B. H. C. production

per  $\gamma$ -B. H. C. 1000kg production,

36% $\gamma$ -B. H. C.	3,240kg
loss	660kg
$\alpha$ -B. H. C.	15,550kg

and

disused Non- $\gamma$ -B. H. C. 1,750kg

#### On the kinds of the industrial manufacture of pentachlorophenol

(1) Synthesis of hexachlorobenzene by means of the chlorination of benzene or mono-, di-, tri-chlorobenzene follows the hydrolysis of the former.

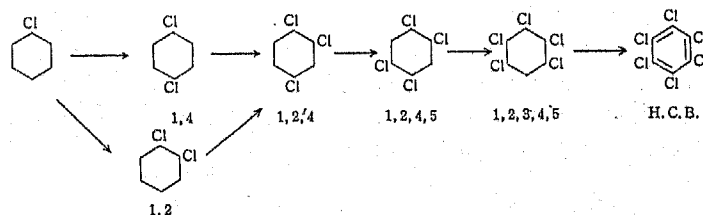
(2) Synthesis of hexachlorobenzene by means of the chlorination of trichlorobenzene which is produced by the alkaline or heat decomposition of Non- $\gamma$ -B. H. C., then hexachlorobenzene is hydrolyzed.

(3) Hydrolysis of hexachlorobenzene which is produced by a triple molecular polymerization of perchloroethylene, trichloroethylene, tetrachloroethane or acetylene tetrachloride.

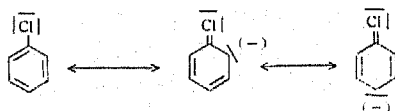
(4) Chlorination of phenol, and so forth.

### CHLORINATION OF BENZENE

The order of chlorination, in the presence of aluminium-mercury couple<sup>3)</sup>;




There are the following phenomena in behalf of the variation of double bonds by the resonance;




A lone pair of Cl appears at the ortho- or para-position of the benzene ring. In the case of chlorobenzene the electron density of the ring is decreased on


the whole because of the induction effect, but chlorine which is likely to associate as a positive reagent to a part of concentrated electrons can be combined to the ortho- and para-positions in which the electron density is increased by the resonance, although the reaction is not more easier than the case of benzene.

**Properties of chlorobenzenes:**


Monochlorobenzene,  Cl; b. p. 132.10~132.12°C, f. p. -45.2°C.


Ortho-dichlorobenzene,  Cl b. p. 179°C, f. p. -17°C;

this is a colourless, oily matter; its volatility can be increased by aqueous vapor.


Paradichlorobenzene,  Cl; b. p. 173.7°C, f. p. 54°C;

this is a colourless crystal, subliming easily; the volatility can be easily increased by aqueous vapor.

1, 2, 4-trichlorobenzene,  Cl; b. p. 213°C, m. p. 17~18°C.

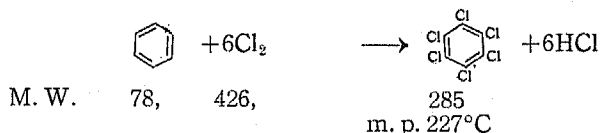
1, 2, 4, 5-tetrachlorobenzene,  Cl; b. p. 243~246°C, m. p. 141°C;

this is a needle-shaped crystal (from ether), subliming easily, being fairly soluble in the cold benzene. This dissolves in CCl<sub>4</sub> far more difficult than the other tetrachlorobenzene. Its chlorination progresses very slowly, and hardly does as a low temperature.

Pentachlorobenzene,  Cl b. p. 275~277°C, m. d. 86~87°C.

this is a long, colourless needle-shaped crystal (from alcohol), easily subliming, being easily soluble in benzene; it is said that the m. p. of this yielded from 1, 2, 4, 5-tetrachlorobenzene is 83~84.5°C.

**Chlorination of benzene:** the reaction;



appears to be for the first time performed by Page (1884)<sup>5)</sup>, and on basing upon his method H. Erdmann did it with ironchloride.

Thereafter it seems to be no useful reference literature about this problem performed in batch system in a liquid phase.

**Example of the experiment:** chlorine 417g. (95.5% of theoretical amount) is passed into the mixture of benzene 78g (1 mole) and Fe 3.5g (10g as FeCl<sub>3</sub>),

the reaction temperature is taken to be higher than the melting point of chlorobenzene at each stage and lower than that boiling point, increasing from the room temperature up to 226°C at the final stage (the m. p. of hexachlorobenzene is 227°C). Since the cooler (outlet) was blocked by a sublimated matter,  $\text{CCl}_4$ , 20g (10g is collected afterwards, the other is lost) was made to drop into the cooler and the wall was washed. The reaction took 9 hours and 45 minutes, the blackmass of a raw hexachlorobenzene 225g was obtained (at the bottom of the reaction vessel Fe, the catalyser, appreciably remained not to be chlorinated), its m. p. being 223~227°C; this was recrystallized with  $\text{CCl}_4$ , 2,500ml and hexachlorobenzene refined was 173g; m. p. 225~228°C (77% yield).

The reaction progressed very smoothly, but even if the author took good care to make chlorine send into the vessel in order to be no unavailable chlorine, on account of the loss of product by being accompanied with HBI gas and by the sublimating properties, chlorine could not be sent into theoretically as above. Hence, the yield of raw product was only 79% and although the contents in the vessel was believed to be almost hexachlorobenzene, it appeared to be a black tarry matter. The loss of  $\text{Cl}_2$  was 2g or more (~0.5%). If no solvent was used to wash the vessel, the exit was frequently clogged, so that it was cleaned and exchanged for a new pipe more than three times.

$\text{AlCl}_3$  is very strong as a catalyst, hence it seems to be likely to cause a by-reaction; moreover since its b. p. is 183°C, it is difficult to use it at the final stage of the reaction with the temperature raised close to the m. p. 227°C of hexachlorobenzene. Besides, if the reaction is performed with a solvent at a low temperature, there is a defect that the rate is slow.

If the chlorination of chlorobenzene reacts violently the vessel should be cooled by cold water. It is said that the reaction from mono- to di-chlorobenzene necessitates two times as much  $\text{AlCl}_3$  catalyst as the reaction from ortho- to tri-chlorobenzene (on starting with the same quantity). The reaction from para- (m. p. 53°C) to trichlorobenzene can be done at 60°C. The reaction from 1,3,5-tri- to tetrachlorobenzene goes on smoothly. The melting points of pentachlorobenzene from tetrachlorobenzene are;

83~84.5°C	from 1, 2, 4, 5-tetrachlorobenzene
83~85°C	from 1, 2, 3, 4-tetrachlorobenzene
84~85.5°C	from 1, 3, 4, 5-tetrachlorobenzene

The order of the rates of chlorination are as follows: 1, 3, 4, 5-tetra-, 1, 2, 3, 4-tetra-, 1, 2, 4, 5-tetrachlorobenzene. It is said that, since 1, 2, 4, 5-tetrachlorobenzene is more difficult to dissolve into  $\text{CCl}_4$ , the dilution has a great effect in the reaction.

Since pentachlorobenzene can be chlorinated rapidly, they say that the majority of the raw product will easily be achieved to the final stage of chlorination.  $\text{CCl}_4$  and benzene can not make an azeotrope. It is said that at the room temperature the chlorination by chlorine gas with trichlorobenzene 182g and  $\text{CCl}_4$  364g can only up to the stage of tetrachlorobenzene.

It is necessary to pass chlorine into a washing bottle of  $\text{H}_2\text{SO}_4$  beforehand, for the moisture greatly affects the chlorination. Iron-scrap seems to be

chiefly used as catalyst for the chlorination of benzene in liquid phase reaction in the industry. If chlorine is passed into benzene without catalyst on exposing in light at a low temperature, an additional chlorine compound is gained. In the chlorination from mono- to dichlorobenzene, para- (65.6%), ortho- (29.6%) and meta-dichlorobenzene are obtained in the case of  $\text{AlCl}_3$  catalyst, and para- (55.8%), ortho- (38.6%) and metadichlorobenzene with  $\text{FeCl}_3$  catalyst.

If benzene with chlorine is passed on a reduced copper, additional compounds are obtained besides benzene derivatives substituted by chlorine. When there exist usual catalysts of chlorination, the substitution takes place invariably at the benzene ring.

When a catalyst (for instance,  $\text{FeCl}_3$  etc.) is used, as above, in the chlorination of benzene and less chlorinated benzene, the reaction comparatively easily goes on, but in the viewpoint of industrial economy it cannot be said to be satisfactory to be done with these only. That is there are some difficult points such as follows:

(1) As the chlorination completes, chlorine becomes unavailing, viz., it comes to pass through out the vessel without complete reaction.

(2) It is necessary to increase the reaction temperature till more than  $220^\circ\text{C}$  for the high melting point of the product, hence it becomes likely to sublime and the processes difficult to operate.

(3) Although these weak points can avoid by means of using anti-chlorination solvents such as  $\text{CCl}_4$ ,  $\text{SO}_2\text{Cl}_2$  or chlorosulfonic acid, there are difficulties that the loss of solvents and the complicated processes of the work are accompanied with these.

#### Chlorination in gas phase

According to P. B. report, the chlorination of benzene in a gas phase is carried out as follows: Chlorination is performed in a quartz tube at more than  $250^\circ\text{C}$  without catalyst. Hexachlorobenzene is stable even at high temperature, and hence a large quantity of the reaction heat can be given to it without uneasiness, and chlorine 380g/hr saturated with benzene vapor at  $60^\circ\text{C}$  and  $\text{N}_2$  360 l/hr are passed into the quartz tube of inner diameter 11mm and of length 76cm. The gases first go through the part filled up by Raschig rings along a length 10~15cm, and subsequently are put in a heating zone at  $500\sim 600^\circ\text{C}$ . Colourless hexachlorobenzene of m. p.  $227^\circ\text{C}$  thus enters at the rate of 214g/hr into two receivers; the yield is 98% and the excess chlorine 15%. Mono-, di- or trichlorobenzene or a mixture of those also can be chlorinated in a similar way to hexachlorobenzene. In the case of using trichlorobenzene as the raw material, the heat evolved in the reaction is little and nitrogen as a carrier is not necessary.

According to our experiment a combustion is prone to occur, some caubonized or tarry matter is produced and if the inflow is accelerated, then the chlorination should be incomplete. Depending on degrees of using inert gas the reaction results in either an incomplete product or a combustion of benzene, and some carbonization cannot be avoided; the management of the control is thus very difficult. If this difficulty of control were overcome, the result is more good than the liquid phase reaction, but indeed this is a serious matter.

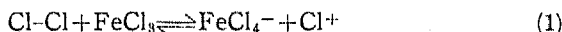
As compared with this point the heat decomposition and the simultaneous chlorination of Non- $\gamma$ -B. H. C. as stated below can be operated by far easily in the view-point of heat balance and moreover it is a strong point that the latter is of the lowest cost price.

#### On the catalyses of chlorination

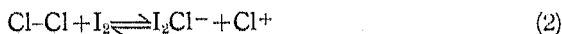
It is desirable to utilize catalyzers for producing polychlorinated compounds. There are two types, viz., radical as well as ionic type in the halogenating reaction of aromatic compounds;

(1) radical type: chlorination of a side chain, additional chlorination to a double bond etc., these are catalyzed by the light.

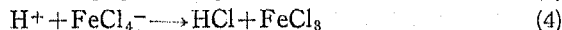
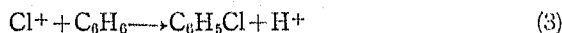
(2) ionic type: it seems to be ionic to substitute an atom on the benzene ring for halogen, and its catalysts are  $I_2$ ,  $Br_2$ ,  $AlCl_3$  etc. It is such a reaction that takes away a halogeno-negative ion from a halogen molecule and discharges a halogeno-positive ion; such that  $H_2SO_4$ ,  $BF_3$ ,  $ZnCl_2$ ,  $TiCl_3$ ,  $GaCl_3$ ,  $SnCl_2$  and  $Al_2Br_6$  etc. have the strong electrophilic properties and convert a halogen molecule  $X_2$  into  $X^+$  ion, hence it can catalyze the chlorination;



or



and



Since a reacting agent is a halogeno-cation ( $Cl^+$ ), it has the orientation property of a substituent, the effect of a substituent on the reaction rate and so on, having the same characteristic as the reaction of the general positive reagents. It is this that chlorine is substituted at the ortho- and para-position of monochlorobenzene

$AlBr_3$  (m. p.  $90^\circ C$ ) and  $GaCl_3$  (m. p.  $78^\circ C$ ) are different from  $AlCl_3$ , being capable to be soluble in various solvents, hence it is convenient in the case where a homogeneous solution is necessary.  $FeCl_3$  is used in the same object as  $AlCl_3$ . It is said to increase the yield of benzylation on mixing a little  $FeCl_3$  as the catalyst.  $BF_3$  is a colourless gas and used in the same object as  $AlCl_3$ , especially in the reaction of alkylation. It has a strong point to avoid the formation of tarry matter by polymerization or condensation of the product, which occurs in the case of  $AlCl_3$  catalyst.

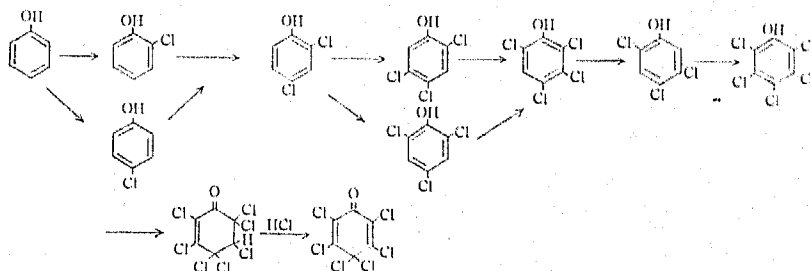
### CHLORINATION OF PHENOL

Upon adding  $Cl_2$  in 1 kg phenol, and after increasing the weight of its content to the point where trichlorophenol has been formed, add 30~40g  $FeCl_3$ ; at  $130^\circ \sim 140^\circ C$  again put  $Cl_2$  into it and when pentachlorophenol is produced completely, discontinue to send  $Cl_2$ ; after cooling the product, shake it with two times petroleum ether, and remove the filtrate. Heat the remainder to remove petroleum ether by distillation, dissolve the all insoluble matter in alkaline water, and 2~3 weight per cent of sodium peroxide and

filter (in order to remove the coloured matter). Make acidic the filtrate with hydrochloric acid, then wash the precipitated pentachlorophenol with cold water, recrystallize with benzene.

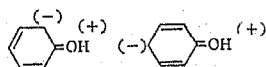
The above reaction progresses easily at 40~70°C up to trichlorobenzene without catalyst; and in order to go on beyond trichlorobenzene, it becomes necessary a proper catalyst. For the reaction of theoretical  $\text{Cl}_2$ , it must be heated up to 150°C, and  $\text{AlCl}_3$  and  $\text{SbCl}_3$  are good catalysts and  $\text{FeCl}_3$  is the next in this case. Pentachlorophenol is refined by a sublimation method or by a method using solvent.

The reaction takes place step by step, but does not cease at pentachlorophenol; it goes on further till the point at which chlorine adds to the double bond of the ring, producing heptachlorocyclohexanon and hexachlorocyclohexachin etc. Attention must be paid not to add over excess chlorine, for these latter reaction rates are large.



It is said that the reason why the chlorination of phenol can easily take place originates from the fact that on account of crowding of negative charges in the ortho- and para-positions in phenol a force of snatching the halogen-cation from a halogen molecule appears. Hence the coexistence of a weak base such as water increases the halogenation velocity as a result of formation of a phenolate-ion, upon promoting the electrolytic dissociation of phenol.

It seems to be that even by the catalyst such as  $\text{FeCl}_3$ , an appreciable reaction of radical type can occur in the chlorination of aromatic compounds, an atomic chlorine then reacting and not the cation, for example, even in the gaseous phase chlorination at 500~600°C 1,3,5-trichlorobenzene chlorinated at the meta-position has been obtained from monochlorobenzene.<sup>6)</sup> They say that -OH of phenol itself as well as  $\text{O}^-$  of phenolate-ion are said to be the radicals which make to crowd electrons by the resonance effect at the ortho- and para-positions. -OH radical is of very little electrophilic nature.

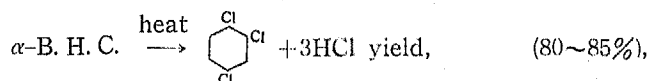


The chlorination of phenol, as stated above, is easily performed in the industrial technique, but the only weak point in its industrialization is its higher price.

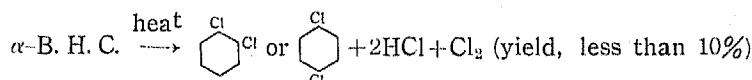


HEAT DECOMPOSITION OF NON- $\gamma$ -B. H. C.

The pure  $\beta$ - and  $\delta$ -isomers do not decompose in the course of 24~27 hours at 110°~120°C, the pure  $\alpha$ - and  $\gamma$ -isomers decompose by 0.07 per cent. B. H. C. of industrial purity decomposed by the amount of 0.25 per cent, but it seems that this is probably because of the trace of catalytic matter in it.<sup>6)</sup>  $\beta$ - and  $\delta$ -isomers are the most stable.  $\alpha$ -B. H. C. starts to decompose near at 220°~230°C only by heating, decomposing fairly rapidly to trichlorobenzene at above 250°C.



by-reaction:

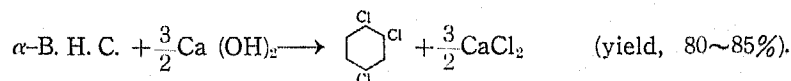


In the heat decomposition in a industrial process there are hard points that the amount of B. H. C. which gets mixed to the product by sublimation of the latter is large, the corrosion of the reacting vessels due to the moisture involved takes place, and also the yield is not too high.

**Decomposition of Non- $\gamma$ -B. H. C. in alkaline medium**

$\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -,  $\varepsilon$ -isomers of  $\text{C}_6\text{H}_5\text{Cl}_6$  produce with high yield only 1,2,4- $\text{C}_6\text{H}_3\text{Cl}_3$  on reacting with N-EtOH-KOH at the temperature of reflux, viz., it is said that from  $\alpha$ -isomer it is 92.1%, from both  $\beta$ - and  $\gamma$ -isomers 99.4%, and with traces of 2,4- $\text{Cl}_2\text{C}_6\text{H}_3\text{OH}$ , 2,4,6- $\text{Cl}_3\text{C}_6\text{H}_2\text{OH}$  and other compounds.<sup>7)</sup> This is thus a favorable one as a reaction process but not economical from the view-point of the cost price of the materials and the complicated steps.

**Decomposition of B. H. C. by lime:** This method is inferior to the decomposition by NaOH;  $\text{Ca}(\text{OH})_2$  reacts at 6 atm. and the yield is 62 per cent, while NaOH gives the yield of beyond 90 per cent of refined trichlorobenzene at 3.5 atm.

**Examples of the decomposition in an alkaline medium****Trichlorobenzene:**

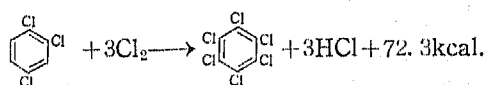
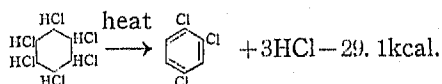
	1, 2, 4-	1, 2, 3-	1, 3, 5-	(temp. of decomposition)	hours
$\alpha$ -isomer EtOH+NaOH	75.9%	17.6%	6.5%	80°C	1
$\beta$ -isomer EtOH+KOH	86.4%	5.3%	8.3%	80°C	4
$\gamma$ -isomer EtOH+KOH	82.4%	4.7%	12.9%	80°C	1

The yield increases in proportion to the time in the case at the same pressure or temperature. In the decomposition of the unavailable B. H. C., an old literature has been stated that the most part of the products are the isomers of 1,2,4- 1,2,3-, and 1,3,5- trichlorobenzene, and the yield was 14~25 per cent, but the later study in U. S. A.<sup>8)</sup> reported that the product was only

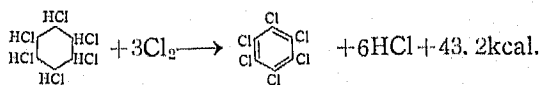
1, 2, 4- trichlorobenzene.

According to Ullmann as well as Beilstein, the properties of trichlorobenzene is as follows; specific gravity 1.45 (20°C); main impurity, 1, 2, 3-trichlorobenzene (below 12%); boiling point 214.8°C and its range 213~217°C; melting point 8~11°C; flash point 100°C; no ignition point; heat of vaporization 58.2 cal/g; specific heat 0.20cal/g; viscosity 1.97 centipoise (25°C).

HEAT DECOMPOSITION AND SIMULTANEOUS CHLORINATION  
OF NON- $\gamma$ -B. H. C.  
IN THE GASEOUS PHASE



The resultant heat evolved by the both reactions is 43.2kcal;



M. W. 291      213      285      219

The results of rectifying distillation of trichlorobenzene (T. C. B.)  
produced by heat decomposition:

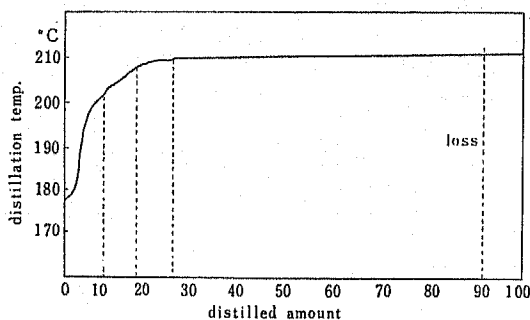


Fig. 1. Distillation curve of a crude trichlorobenzene by Fenske's rectifying column

F. A. Gunther (1947) proposed that T. C. B. which is produced from the heat decomposition of B. H. C. is only 1, 2, 4-isomer, but from above results of rectification it is seen that it is not a single product.

**Table 1.** Data of fractional distillation by Fenske's rectifying column and data from references

fraction	Beilstein	international critical Tables	crude T. C. B.	174° ~200°	200° ~207°	207° ~209°	the remainder
				10%	12.7%	72.1%	3%
$d_{25}^{25}$	1.4634	1.4460	1.4480	1.3650	1.4280	1.4565	—
$n_D^{25}$	1.5524	—	1.5680	—	1.5635	1.5682	—

**Table 2.** The purity of 1,2,4-isomer after farther rectifying distillation of the fraction between 208~209°C

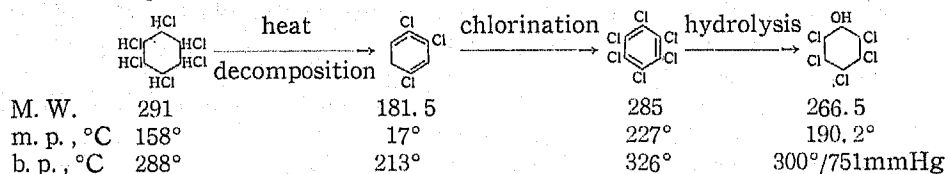
	208~209°C	first running	principal fraction	last running
fraction ratio		1	4	1
1,2,4-isomer	87.6%	84.8%	88.8%	84.7%

**Table 3.** The results of elementary analysis and other data about each fraction from the rectification of T. C. B. yielded by the heat decomposition of B. H. C.

	fraction of T. C. B.				data from Beilstein			
	No. 1	No. 2	No. 3	No. 4	1,2,4- T. C. B.	ortho- D. C. B.	meta- D. C. B.	para- D. C. B.
temp. range, °C	174~200°	200~209°	207~209°	remai- nder	b. p. 214.8°C	b. p. 179°C	b. p. 173°C	b. p. 174°C
composition, % or b. p., °C	10%	12.7%	72.1%	3.3%				
Specific gravity distillate dehydrated	1.3650	1.4280	1.4565		1.4634	1.3280	1.2830	1.458
	1.3075	1.4146	1.4551		1.4460			
$n_{25}^{25}$	—	1.5675	1.5682		1.5524			
analyzed Cl, %	48.78	55.3	58.06		theore- tical 58.64	theore- tical 48.26	theore- tical 48.26	theore- tical 48.26
presumptive compounds	D. C. B.	D. C. B. + T. C. B.	T. C. B.					

From above it is seen that the first running of trichlorobenzene produced by heat decomposition is dichlorobenzene. Hence inferring from the melting point of the heat decomposed product, it is not allowed to suppose for the composition of the product to be a mixture of trichlorobenzene isomers. According also to the elementary analysis the first running from trichlorobenzene is shown to be dichlorobenzene.

#### The example of the reaction



## (1) Apparatus:

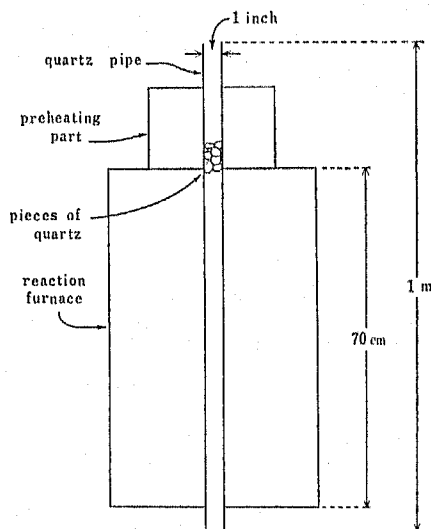


Fig. 2. Outline of reaction furnace

(2) **Reaction:** after heating the quartz tube (Fig. 2) to  $600\sim 650^{\circ}\text{C}$ , the mixture of the unavailable B. H. C. 1 vs. chlorine over 3 in mole ratio (the excess portion is about 20~30 weight %) being passed into it, then B. H. C. is decomposed by heat and at the same time chlorinated with no carbonization and no production of tarry matter, the crude hexachlorobenzene (m. p.  $224^{\circ}\sim 227^{\circ}\text{C}$ ) being obtained with the yield 98~99 per cent.

The method of addition of B. H. C. to fall into the quartz tube is performed by dropping as it is powder or after it is melted. In the case of the latter the sublimation is apt to result in blockading the entrance, so that this difficulty must be skilfully avoided. If B. H. C. is added as it is powder, it seems once for B. H. C. smoothly to fall into the quartz tube at first sight, without delay a hot wind or the hot chlorine gas which comes up along the tube moistens B. H. C. to be subsequently added, making it difficult to fall smoothly and give nonuniformity to the addition velocity of B. H. C. at the initial and the final stages of the reaction. Further since hexachlorobenzene produced has the subliming nature, it is apt to blockade the exit. Even the temperature from  $500^{\circ}$  to  $550^{\circ}\text{C}$  is still hard for the reaction smoothly to advance, though it is free from the care of high temperature because hexachlorobenzene is stable for it. There is of course a limit for the falling velocity of B. H. C. because if it falls too fast the reaction does not carry out completely, namely unreacted B. H. C. comes out at the exit or the crude products ended only in lower membered chlorobenzenes are obtained.

## (3) Experiments:

In these experiments in laboratory scale because of the method used which dropped B. H. C. as it was powder by a screw the falling velocity was not uniform and the amount of reacting B. H. C. also was not so all along, of

**Table 4.** Data of heat decomposition and simultaneous chlorination of B.H.C. (added with powder)

B.H.C., g	Cl <sub>2</sub> , g	Cl <sub>2</sub> , %	H. C. B., g	yield of reaction		reaction temp., °C	m. p. °C	colour
				H. C. B.	time, hour			
135	178	180	129	97.8	1	600	225.2 ~227.3	light gray
52	76	199	50	98.0	1	"	225.2 ~227.8	light gray
160	167	142	152.5	97.2	1	"	224.0 ~227.2	ash
110	113	141	104.5	97.2	1	"	223.7 ~227.8	light gray
185	188	139	178	98.1	1	"	222.8 ~227.1	ash
84	85	138	79.5	96.7	1	600	222.8 ~225.8	light gray
96	69	125	90.5	96.2	1	650	221.4 ~224.5	dark gray
187	166	121	174	95.2	1	600	220.0 ~225.8	dark gray
91	88	132	83.5	93.8	1	550	195.8 ~218.8	yellowish white

cause it is probably able for falling condition to be uniform to some extent in the industrial scale and by means of the technique of the chemical engineering.

The falling velocity, 90~110g/hr, of B.H.C. gave at 500~550°C lower membered chlorobenzenes, the yield and the melting point being both low. In the variation of the falling velocity of B.H.C. from 50 to 187g/hr the yields and the qualities of the products were all the same grade, but if it was faster than those the reaction became violent, and it seemed probably from this reason that the colour of the products appeared to grow stronger.

The value of the excess amount, that is, from 20 to 30% of chlorine, did not come from the reason on the reaction condition itself but from only the fact that since the adjustment of the addition velocity of B. H. C. could not be made uniform in this experimental apparatus, it was excessively added empirically in order to give the stoichiometrical chlorine throughout. According to P. B. report in the chlorination of trichlorobenzene a diluent is not necessary, but in our reaction the heat is absorbed in the course of the decomposition of B. H. C., hence the fear of the combustion is much less in our case than the case of the starting from trichlorobenzene itself. This is because the heat evolved by the chlorination should be absorbed by the heat decomposition of B. H. C. (endothermic reaction), therefore, the reaction will advance with ease from the view-point of the heat balance.

The raw B. H. C. which was sorted out beforehand from dusts, cotton-wastes and granular or masslike B. H. C. was used, because otherwise B. H. C. was not smoothly dropped as it was powder. Moreover a dried B. H. C. was needed, for it involved the moisture and hence adhered to the screw for conveying B. H. C. powder.

Every part of the quartz tube is necessary to be heated upon taking into consideration the heat for the chlorination and that which is necessary to the decomposition of B. H. C., and the appropriate temperature distribution and an allowance of the lagging material to maintain it are needed. Pieces of

quartz were moderately filled up in the upper part at 600°C of the tube because otherwise B. H. C. dropped spontaneously and arrived directly at the not heated, lower part of the tube without reaction with chlorine. It is necessary to fill up the tube only with chlorine directly before and after the reaction, otherwise lower membered chlorobenzenes or carbonized matter will be produced.

(4) **The Relation between Dropping velocity of B. H. C. and the Temperature Distribution:** the upper part of the reaction tube, from which the heat is snatched away as the heat of fusion of B. H. C. as well as the heat to increasing the temperature of chlorine, and also for the necessity of the endothermic decomposition resulted in dehydrogen chloride, shows for the temperature at that part to fall gradually as the reaction goes on. The temperature at the middle part of the tube increases by the exothermic chlorination reaction. In the lower part there is almost no production of heat, and since the heat is transferred only by the travelling of the product, the temperature increase is not so great; it falls gradually along with the lower part by the radiation of heat at the exit. If the heating the middle part of the reaction tube is removed the higher part of the temperature distribution travels to the lower part with time; this is increased with the increase of falling velocity of B. H. C.

The following Table 5 shows that the temperature to 790°~800°C has no influence upon the product and any carbonization does not occur; a yellowish white product of m. p. 225°~227.2°C has been obtained.

Table 5. Data from a Test Plant.

B. H. C., kg/hr.	Chlorine		Hexachlorobenzene				temperature distribution	
	kg/hr.	%	kg/hr.	yield, %	colour*	m. p., °C	minimum	maximum
13.5	12.7	129	12.0	91.0	yellowish white	224.9 ~227.0	180~200	750~770
13.0	12.4	130	11.7	91.8	"	224.2 ~227.2	—	—
16.3	15.6	132	15.2	95.3	brownish white	224.1 ~227.5	150~170	770
12.7	14.2	153	11.8	95.0	yellowish white	225.1 ~227.2	180	790~800

\*Colour having a tinge of yellow is due to chlorine gas, and upon drying after washing with water all of these become white.

(5) **Explanation of Experiment:** if the falling velocity of B. H. C. is large to some extent, the product gets colored with light brown or blackish brown. On the contrary if it is small, it appears for B. H. C. to become a stable hexachlorobenzene smoothly and easily, the product of high melting point being obtained even at a high temperature with no decomposition and no carbonization. In the testing plant at 550°C the melting point of the product was 217~223°C which was almost similar to the results of laboratory experiment. In this apparatus the falling of H. B. C. which was not very uniform required the excess in chlorine to be 30 per cent more than the theoretical amount. It appeared that some quantity of nitrogen which was used as a

diluent of chlorine did not influence on the melting point of the product.

Since the melting point of  $\gamma$ -B. H. C. is lower ( $112^{\circ}\sim 113^{\circ}\text{C}$ ), in the reaction where B. H. C. involving  $\gamma$ -B. H. C. is dropped as it is powder the B. H. C. to be dropped becomes sticky for the ascending hot wind and successive dropping of B. H. C. gets to be more difficult than the case of Non- $\gamma$ -B. H. C.

### SYNTHESIS OF PENTACHLOROPHENOL WITH HEXACHLOROBENZENE

**An example;** hexachlorobenzene (m. p. over  $225^{\circ}\text{C}$ ) 95g and NaOH 34g (mole ratio of 1:2.5) were mixed with methanol 213g (13.5% solution), and made these react at  $135^{\circ}\text{C}$ . The reaction pressure became  $11.5\text{kg}/\text{cm}^2$ . Upon completing the reaction the product was cooled, the crystal precipitated was filtered, and methanol used was collected from the filtrate: the precipitate obtained from the latter procedure was added to the crystal already obtained, these were dissolved into  $\text{H}_2\text{O}$  500 ml., the undissolved material was filtered, the filtrate was acidified (congo red), the crystal precipitated in this way was washed with water, and this raw product was recrystallized by benzene; the resultant material after reaction were 332g, the loss 3%, a recollected methanol 168g, the yield of recollection 79.3%, an undissolved material with alkalinity 3.5g, a raw product 79g, the yield 88.9%, the melting point of the raw product  $157^{\circ}\sim 173^{\circ}\text{C}$  (that of technical grade  $159^{\circ}\sim 178^{\circ}\text{C}$ )

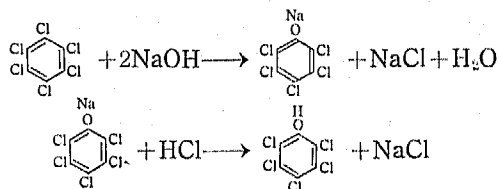
Recrystallization:

fractions	ppt. from filtrate, 'g	m. p., $^{\circ}\text{C}$	yield, %
first	38	174~182	48.2
second	17	151~173	21.5
third	10	103~134	12.7
remainder	5	52~ 67	6.3
loss	9		11.3
total	79g		100%

Upon summing up the first and the second recrystallized materials (55g), this is once more recrystallized as follows:

first	43	181~183	78.2
second	4	132~152	7.3
remainder	6	52~ 69	11.1
loss	2		3.4
total	55g		100%

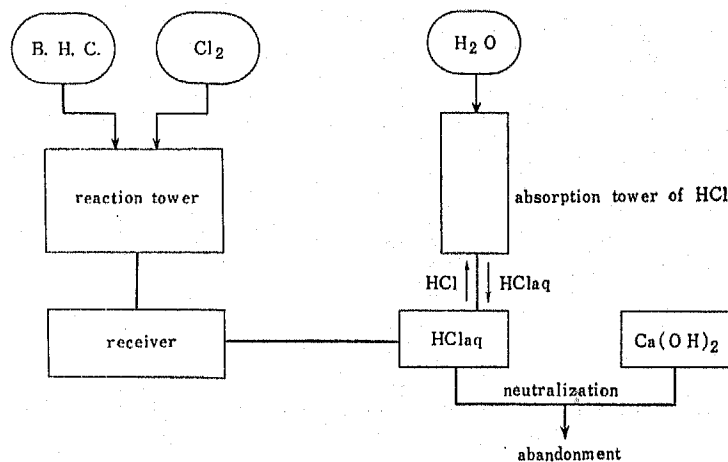
By the way the meltig point of the pure pentachlorophenol is  $190^{\circ}\text{C}$  and that of its monohydrate  $174^{\circ}\text{C}$ . The equation of reaction is as follows;



Hexachlorobenzene (m. p. 223°~227°C, greyish white colored) which was produced as stated above from Non- $\gamma$ -B. H. C. with chlorine at 600°C was used to manufacture pentachlorophenol with the pressure 6.5kg/cm<sup>2</sup>, at 115°C and for 12 hours, for four times, resulting in the following: the yield of pentachlorophenol 93~94 %; the purity 97.2~100 % (the mean 98.6 %); the mean recollection yield of methanol 84.7 %; an undissolved matter in alkaline solution 8.2 % of hexachlorobenzene; m. p. 156°~175°C; weak orange color. Compare with the results which were obtained with the refined hexachlorobenzene, and these were the following: the yield of pentachlorophenol was 95 %; the purity 98 %; an undissolved matter in alkaline solution 5 %; m. p. 160~178°C; almost white color.

The Na-salt of pentachlorophenol is obtained with theoretical yield at the temperature of dissolution 70°C with the mole ratio;

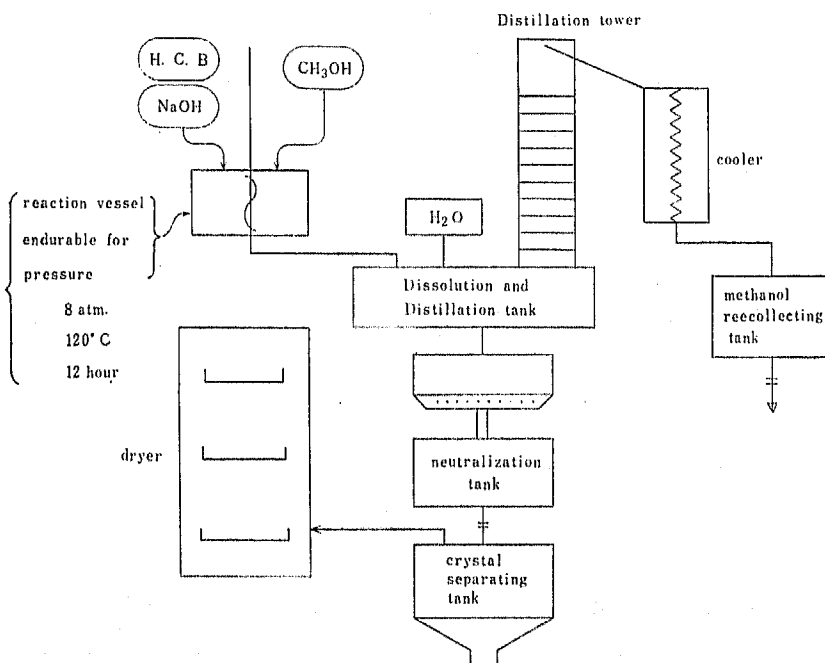
pentachlorophend: NaOH=1:1.1.



THE ILLUSTRATION OF THE INDUSTRIAL PROCESS OF THE DECOMPOSITION OF NON- $\gamma$ -B. H. C. (THE UNAVAILABLE B. H. C.) BY HEAT AND THE SIMULTANEOUS CHLORINATION

The Flow Diagram of the Industrial Process of the Synthesis of Pentachlorophenol from Hexachlorobenzene





### SUMMARY

In this paper, the kinds of the process of manufacturing pentachlorophenol are mentioned first, then the conditions of chlorination of benzene by chlorine gas in liquid-gas (inhomogeneous reaction) and gas phases are stated in detail, and the author pointed out the difficulties of these both methods compared to the next mentioned way which uses the heat decomposition and the simultaneous chlorination of Non- $\gamma$ -B. H. C. from view points of the low cost price of the latter and the heat balance of the reaction. By the way alkaline decomposition of B. H. C. to produce trichlorobenzene is stated and this way also concluded to be inferior to the last method. The chlorination of phenol is an easy one but inferior to the above method in the view-point of the cost price in such a factory not to manufacture phenol.

Such being the case the author propose that the method of the heat decomposition and the simultaneous chlorination of Non- $\gamma$ -B. H. C. whose reaction the author treated and accomplished for the first time (1952) is one of the best way to produce pentachlorophenol in a manufacturing industry peculiarly in such a factory dealing with B. H. C., and he states the detailed method of this reaction.

## REFERENCES

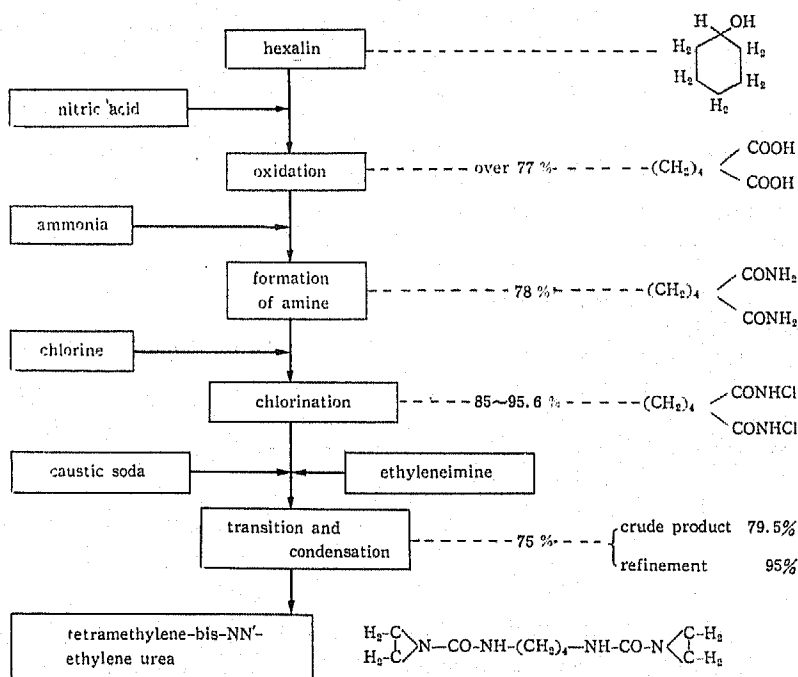
- 1) H.L. Haller, I.E.C., **39** (1947), 467~473
- 2) K.C. Kauer, R.B. Du Vall and F.N. Alquist, *ibid* 1335
- 3) J.B. Cohen and P. Hartley, J. Chem. Soc. of London, (1905), 1360
- 4) E.H. Huntress "The preparation, properties, chemical behavior and identification of organic chlorine compounds" John Willey press, New York
- 5) A.G. Page, Ann., **225** (1884), 196
- 6) Muller, "Neu. Auschau". p.205
- 7) F.A. Gunther and R.C. Blinn, J.A.C.S., **69** (1947), 1215-16
- 8) F.A. Gunther, J.Econ., **40** (1947), 874-7

### III Production of Ethyleimine as the raw Material for the Manufacture of Tetramethylene -BIS-NN'-Ethylene Urea

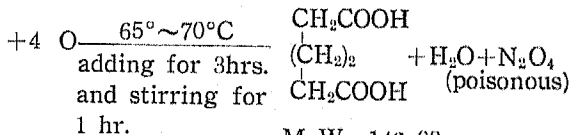
#### INTRODUCTION

In the process of the production of tetramethylene-bis-NN'-ethylene urea, the most difficult point exists in the synthesis of ethyleneimine as a raw material of the former. The author takes aim at the obtaining of the highest yield of ethyleneimine of such a concentration that is necessary to tetramethylene-bis-NN'-ethylene urea and thus the economical process for the manufacturing industry of the latter.

#### PROCESS OF THE SYNTHESIS OF TETRAMETHYLENE -BIS-ETHYLENE UREA



$\left\{ \begin{array}{l} \text{m. p. over } 122^\circ\text{C} \\ \text{an undissolved matter in} \\ \text{water does not occur by the} \\ \text{heating test at } 95^\circ\text{C for 2 hours} \end{array} \right.$

**Each step for the process****(1) Synthesis of adipic acid from cyclohexanol:**1 mole      5.2mole HNO<sub>3</sub> (57)%

M. W. 100

b. p. 160.6°C

(155~170°C for industry)

m. p. 25.5°

sp. gr. 0.9463 (22.6°C/4°C)

n<sub>D</sub><sup>20.7</sup> 1.46542

M. W. 146.08

b. p. 265° (100mmHg), m. p. 151°C

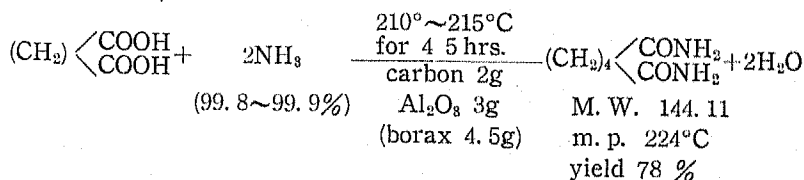
filtered by an ordinary

filter paper by Büchner's filter,

yield over 77 %

**(2) Synthesis of adipicdiamide from adipic acid:**

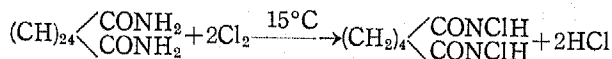
(1 mole is used)



Producing method of adipamide is as follows: add about half an amount of ammonia water to adipic acid, make it a hot solution, then with passing gaseous ammonia into this solution heat it to 200°~220°C and make them react so far that water is no more distilled out. Upon recrystallizing by water the yield of adipamide of melting point 220°C is about 80 per cent. They say that borax or ammonium molybdate are suitable as the catalyst.

**(3) Synthesis of Adipic-NN'-dichlorodiamide from Adipicdiamide:**

(1 mole + 2.4 l water)



M. W. 213

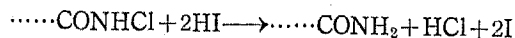
m. p. 145°~147°C (the point of decomposition)

being taken with filter paper

yield 85 %

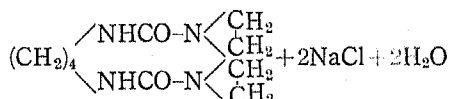
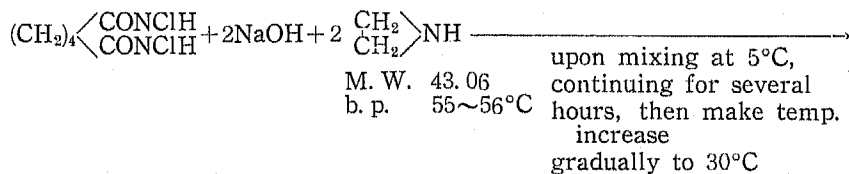
Chlorination of diamide is said that it is not a simple additional reaction of Cl<sub>2</sub> as it stands, but is the reaction of HOCl which is produced in water.

Analysis of chloroamide appears to be analysed by titrating iodine with sodium thiosulfate, in this case the former is produced by potassium iodide solution as follows:



(4) Synthesis of tetramethylene-bis-NN'-ethylene urea from adipic NN'-dichloroamide:

1 mole is added as it is powder



M. W. 226

m. p. over  $122^\circ\text{C}$

yield 75%

(crude product 79.5%, on refining 95%)

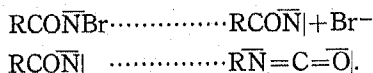
By way of above four processes tetramethylene-bis-NN'-ethylene urea is obtained; well, among these processes the most difficult point exists in the fourth process; we will state something about this process below.

#### ON THE REACTION AMONG ADIPIC DICHLORODIAMIDE, ETHYLENEIMINE AND CAUSTIC SODA (THE FOURTH PROCESS)

##### Mechanism of Hofmanns' reaction<sup>1)</sup> and the properties of diisocyanates

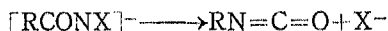


The mechanism, which has been mostly accepted, that N-haloamides give with alkali unstable salts is such that, because of the formation of the unstable one-valenced nitrogen compounds which receive a rearrangement to give isocyanates, HX (where X is a halogen) is removed; however, the author can not accept this interpretation, since, in the first place, it cannot be balanced from the view-point of the binding energy and moreover there should not exist an unstable compound which has no octet structure. Therefore, strictly speaking, it appears that it is not true to describe the reaction equation as follows:



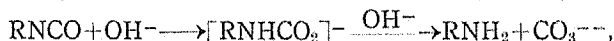
As a molecular complex which has an internal structure of a complete molecule travels along the potential energy valley laid along the decomposition coordinate, the separation of a halogen ion would advance at the same time. From a view-point of the isolation of an alkali salt of a bromoamide, the reaction implies that, first, a nucleophilic reagent removes hydrogen as a proton, then the rearrangement takes place with loosening of a halogen ion<sup>2)</sup>. The easiness of the rearrangement would depend on the velocity of remove-

ment of a halogen ion in the coexistence of alkali. It is proved in regard to the molecule which has an optical activity that a transferring radical never combines with other molecule (intramolecular rearrangement) and also a stereochemical configuration is held in the course of reaction. According to a measurement there decreases the electron density of N atom, to which Br atom adheres, by an electrophilic radical, so that the more difficult becomes Br<sup>-</sup> ion to be separable the more diminishes the velocity of rearrangement, thus the reaction:



results in a rate-determining step.

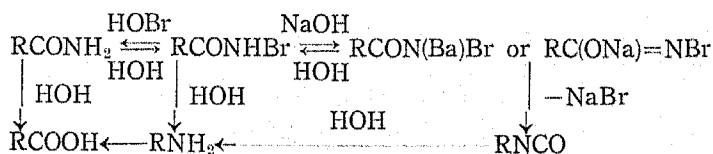
Being dissolved in NaOH solution halogenamide produces Na salt, (RCONBr)Na, and the latter loosens Br<sup>-</sup> ion and rearranges to an isocyanate. Moreover in the case of coexistence of water and excessive alkali it is hydrolyzed to a primary amine:



in an alcohol solution this turns into a urethane:



Being also hydrolyzed a halogenamide may become to the corresponding acid, then the following illustration may be supposed;



Hofmann's rearrangement seems ordinarily to take place at 30°C. The observed values in the above illustration are said that amines are produced from bromobenzamides with the yield 90 per cent at 30°C, and the corresponding acids are given below 5 per cent. In the case of meta- and para-nitro-derivatives they say that the yield of corresponding acids are 25~40 per cent.<sup>2)</sup> Isocyanate and ethyleneimine quantitatively react in an organic solvent at 0°C, it seems to be experienced that the velocity of the rearrangement has a higher temperature coefficient than the addition reaction of ethyleneimine to isocyanate and the hydrolysis.

It has been mentioned that, for instance, the influence of the reaction temperature showed the yield 90 per cent of para-nitroaniline upon dissolving para-nitrobenzamide in an alkali at the boiling temperature using a bath, while the only yield 48 per cent of amine at 30°C<sup>2)</sup>.

According to our experiments the yield of raw product in the above fourth process is raised by 21~26 % by means of the increase of temperature from 25° to 30°C, and also the yield elevated by 16~21 per cent by means of the augmentation of NaOH concentration from 10 to 15 per cent. Now in the case where NaOH is used by 10~25 per cent more excessively than the theoretical amount, the following are shown;

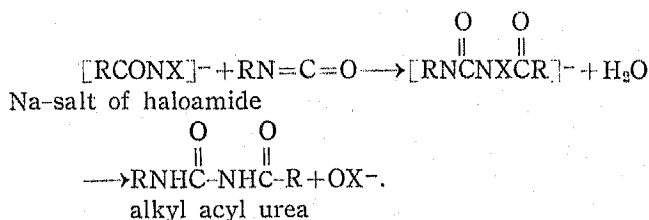
when the concentration of NaOH is 10 %, 30°C is necessary for tht

	final temp.	
“	15%, 27~30°C	“
“	20%, 25°C	“
“	over 25%, the yield does not differ too much at 25°C.	

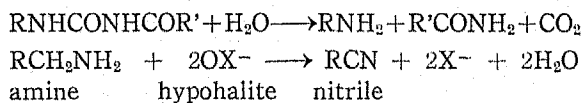
The materials obtained in this case, however, are taken as the following, viz., when the raw products whose yields were 70~85 per cent were treated at 95°C for one hour, the property of tetramethylene-bis-ethylene urea was lost, but in regard to that material which was obtained upon refining the above raw product by means of dissolving in  $\text{CHCl}_3$  and precipitated by  $\text{CCl}_4$  with the yield 72~73%, then even after this heating test at 95°C for two hours the property of tetramethylene-bis-ethylene urea was not lost.

Hofmann's reaction is one that eliminates a carbonyl group from amides, while the fourth process used in this case is one that without eliminating carbonyl group is transferred to the addition reaction with ethyleneimine in a half-way of Hofmann's rearrangement.

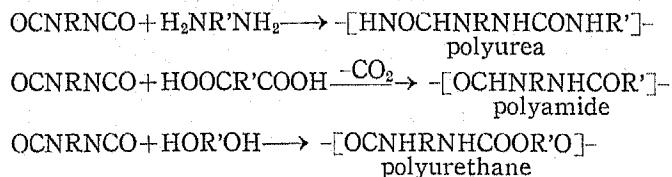
As a by-reaction of Hofmann's reaction, upon reacting with Na salts of haloamide, isocyanates give salts of alkyl acyl ureas in the case of no existence of an excess alkali, and moreover turn to ureas themselves by hydrolysis:



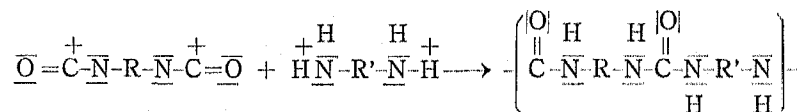
Isocyanates come from higher aliphatic amides react faster with salts of haloamides than with  $\text{H}_2\text{O}$  or alkali, so that they usually give only a little expected amines. Amines are derived from the hydrolysis of alkyl acyl ureas, and by the coexistence of an excess hypohalite most of amines are apt to oxidize to nitriles.



In the higher aliphatic amides and a number of acyclic amides the formation of alkyl acyl urea is usually most strongly apt to take place. The following polymers which use diisocyanate as a raw material can also be produced:



The addition polymerization reaction of these diisocyanates with diamines is as follows:

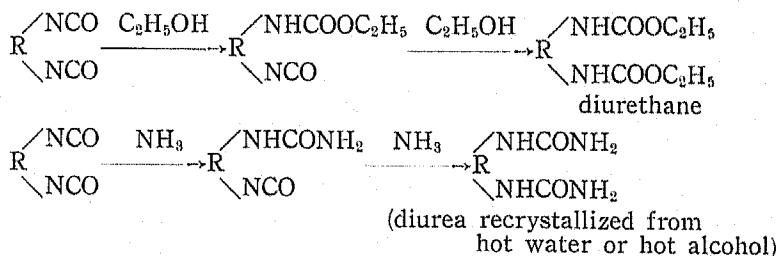


Tetramethylene diisocyanate is a colorless, transparent liquid at the ordinary temperature; upon reacting with a large quantity of water with vigorous stirring a majority of it turns to ring tetramethylene urea (m. p. 172° ~173°C); this also reacts with the moisture in the air. This is a liquid with stimulative odor of boiling point 93° (7mmHg) and 189°C (18mmHg); it is in general produced by the vacuum distillation with a high degree of low pressure. This produces a white precipitate (m. p. 352°C) with the moisture in the atmosphere, and is dissolved in phenol and formic acid;

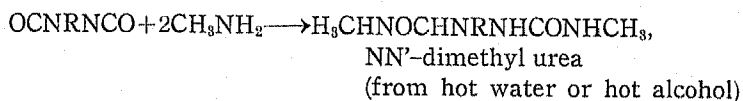


The reaction of diisocyanate with water is complicated;  $\omega$ -amino alkyl isocyanate produced in a midway of the reaction gives rise to either an intermolecular or intramolecular reaction, resulting in polyurea or cyclic urea.

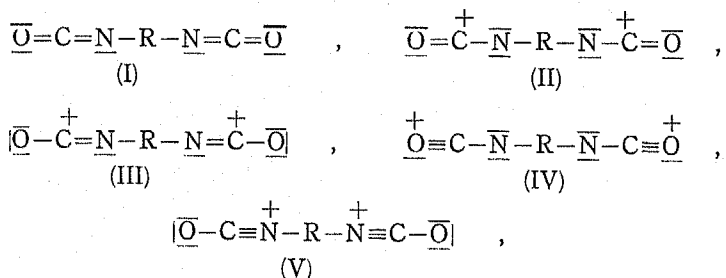
#### Reactivity of diisocyanates:



This formation of diurea takes place rapidly and quantitatively. This and the following reaction:



which takes place instantaneously, are convenient for the detection reaction about polymethylene diisocyanate. The following five resonance structures are to be supposed with regard to diisocyanate:

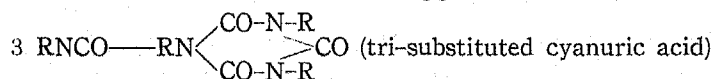
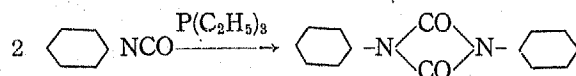
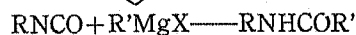
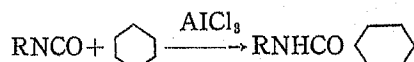
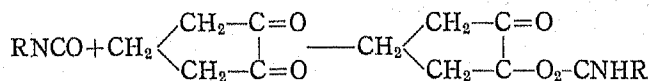
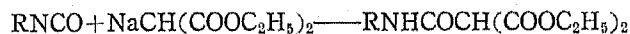
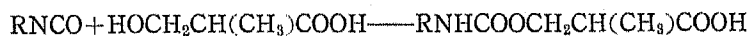
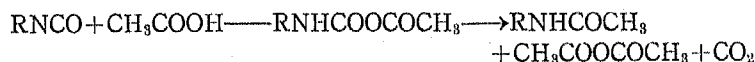
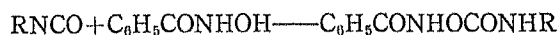
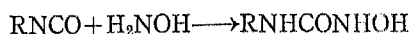
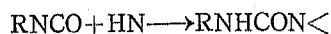
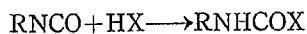




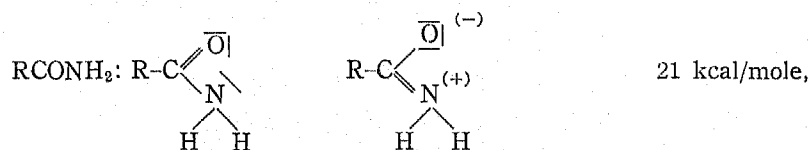
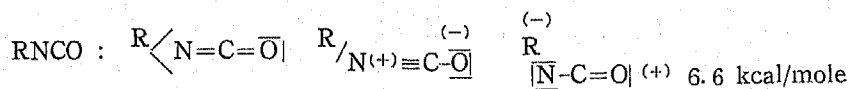
they say that the form (II) is prevalent in alkaline, while not in acid.

Similar to ketene having the like structure, isocyanate is very reactive, reacting vigorously with various kinds of functional groups; the longer the chain the slower it reacts with water, octadecyl isocyanate, for example, is stable in water for several days, giving an emulsifying state; on the contrary the shorter the chain the easier it reacts with water, it is presumed that diisocyanate is particularly reactive with water.

Other reactions of isocyanates, for instance, are as follows;



Resonance energy<sup>3)</sup>:



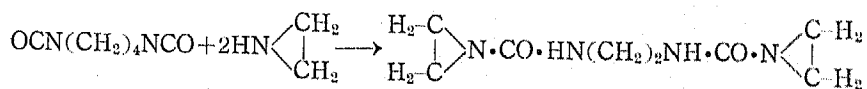
where  $\text{R} = \text{---CH}_3, \text{---C}_2\text{H}_5$ .

#### Reaction between ethyleneimine and polymethylene diisocyanate

This reaction is exothermic, and it is convenient to use solvents or dilue-

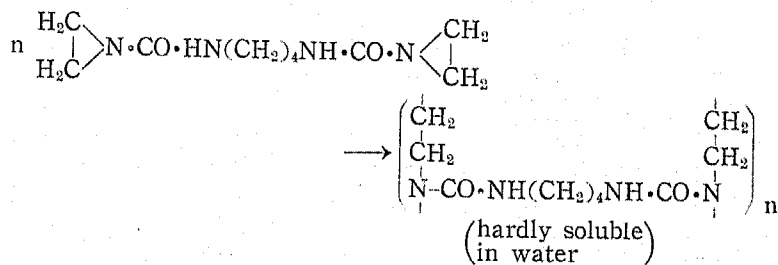
nts; for this purpose anhydrous acetone or petroleum ether is used. Addition is made below 10°C as cooling with ice, and the reaction is carried out at 0°C. The reaction takes place almost quantitatively. Ethyleneimine which is stored for a long time involves its polymer, and the addition compound shows hygroscopic property, becoming soluble in acetone, and has a property to polymerize. This polymer is not soluble in water. Therefore, it is necessary to use one which is newly refined by rectifying distillation.

Even if pure ethyleneimine is used, an insoluble matter is produced by the heat of reaction, hence it is necessary to cool it in the course of reaction. Polymethylene-bis-ethyleneurea which has methylene radicals up to four and six is not soluble in water, but that which has eight is hardly soluble in cold water. Since these are insoluble in anhydrous ether, the washing by ether is used for the refinement and drying of them.



Tetramethylene-bis-NN'-ethylene urea is a white crystal, melting point 124°C, and the yield is over 90 per cent.

Polymethylene-bis-ethylene urea opens its ring and becomes a polymer at 120°~130°C, this being soluble in water, and stored stably for a long time.



#### Properties of adipicdichloroamide (Cl·HN·CO·(CH<sub>2</sub>)<sub>4</sub>·CO·NH·Cl)

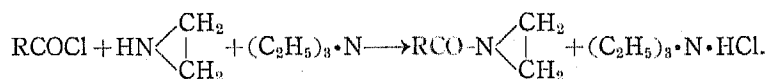
Upon boiling with water or hydrochloric acid this is reduced to the original amide H<sub>2</sub>N·CO·R·CO·NH<sub>2</sub>; dissolving in alcohol and upon being slightly heated with KOH it produces a diamine H<sub>2</sub>N-(CH<sub>2</sub>)<sub>4</sub>-NH<sub>2</sub> by Hofmann's rearrangement. It is soluble in water, methanol, ethanol and acetic acid (but not easily soluble), hardly soluble in ether, and insoluble in petroleum ether, benzene and ligroin, white amorphous crystal of melting point 145°~147°C (decomposition point).

#### Properties of ethyleneimine

Boiling point 55.8°;  $D_4^{26}$  0.8371;  $n_D^{20}$  1.413; vapor pressure 61mmHg at 0°C; specific heat 0.592; heat of vaporization 8,086kcal/mole; heat of formation -21.67 kcal/mole. Ethyleneimine can mix with water at any proportion and appears to be a nitrogen homologue of ethylene oxide, they having analogous properties with each other with the exception of the additional hydroxyl group. Ethyleneimine produces with excess hydrochloric acid a salt which corresponds to the salt of ester of monoethanolamine; for example,

ethyleneimine produces chloroethylamine chlorohydrate with 2HCl.

When a solid NaOH is added to an aqueous solution of ethyleneimine and the latter is stirred, ethyleneimine is separated to the upper layer. Ethyleneimine has an odor like ammonia; it is a very poisonous liquid and is extremely apt to burst. Its molecular refraction is 12.82, while as a ring molecule it is theoretically 12.84 and as a chain molecule it becomes 14.39. Ethyleneimine reacts like a secondary amine as it is a ring molecule, but its ring is also extremely liable to open, so that it is apt to polymerize. Moreover the following reaction is possible:

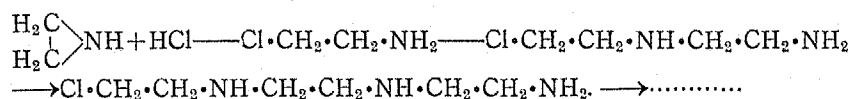


The reactions of ethyleneimine are classified to three main divisions:

- (1) Acylation and alkylation with halogen compounds.
- (2) Acylation and alkylation by means of addition reaction.
- (3) Reaction accompanied by chain opening.

Ethyleneimine is stored with the coexistence of solid NaOH; the polymerization is catalyzed by metals, so that the vessels which are used at the time of manufacturing and storing are preferable to be made of pure iron or steel not involving copper, manganese and nickel etc. The vapor of ethyleneimine attacks the skin, eyes, the respiratory organs and the kidney; the skin becomes inflamed with blisters; similarly the liquid does so too.

**Polymerization catalyst of ethyleneimine:** These are acid sodium sulfate, hydrochloric acid, silica gel, active carbon, chloroethylamine, CO<sub>2</sub> and ethanolamine ester of sulfuric acid. The polymers of ethyleneimine are from viscous one to solid polymer like wax:



Polymerization of ethyleneimine is carried out in the range from the ordinary temperature to 110°C with solvent, with diluent or ethyleneimine only.

**Example of polymerization:** 10 per cent aqueous solution of ethyleneimine is left as it is with the coexistence of one per cent NaHSO<sub>4</sub> for twelve hours at the ordinary temperature, then a material which is colorless, viscous and soluble in water is obtained. If this is performed anhydrously, a colorless solid polymer is obtained. Alternatively, when this is carried out with soaking cellulose in the imine solution, the polymerization occurs in the inner part of the cellulose, a nitrogenous cellulose being obtained.

Upon using 30 per cent HCl as a catalyst, pour ethyleneimine gradually into a vessel having a stirrer, and at the same time make it polymerize violently at 50°~100°C, then an extremely viscous polymer is obtained. Upon mixing 100 parts of ethyleneimine and 3 parts of ethanolamine ester of sulfuric

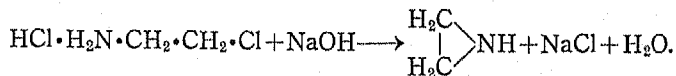
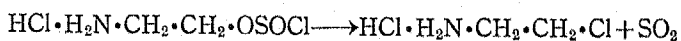
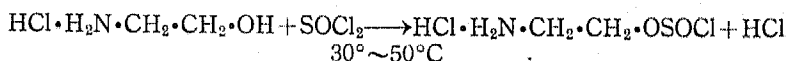
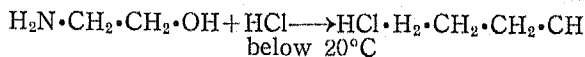
acid, compress and heat them, then a tough polymer like gum is obtained; this is used to give a softness to artificial leathers etc.

In I. G. they say that, when ethyleneimine is added upon using 0.1 per cent  $\text{CO}_2$  as a catalyst, gradually into a little ethylenediamine of temperature  $90^\circ\text{C}$ , according to the addition velocity as well as the concentration of a catalyst polymers of different molecular weights are obtained. Polymers of ethyleneimine is no more poisonous.

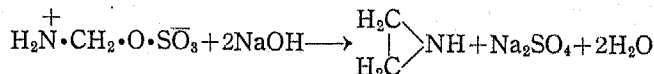
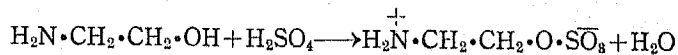
### MANUFACTURE OF ETHYLENEIMINE

There are two way to manufacture with monoethanolamine:

(1) There is a method operated in the early stage at Ludwigshafen as a testing plant with the production of five to six ton per month such as the following; viz.,  $\beta$ -chloroethylamine hydrochloride is first formed, then from this intermediate hydrogen chloride is removed:



(2) This is one developed at Höchst plant in I. G. in a laboratory scale that  $\beta$ -aminoethyl acid ester of inorganic acid is made as an intermediate as follows;



#### Production of ethyleneimine via the intermediate of Beta-aminoethyl acid ester of sulfuric acid

According to P. B. report<sup>4)</sup> of I. G. the yield of ethyleneimine from Beta-aminoethanol is as follows:

$$94 \times 85.5 = 80.3\%; \text{ purity } 99\%.$$

The yield which the author was obtained is the following:

$$80.0\%; \text{ purity } 98.4\%,$$

where he used alkali in his experiment approximately 60 per cent of I. G. Moreover he manufactured ethyleneimine from monoethanolamine so as to be a satisfactory concentration of aqueous solution of ethyleneimine (ca. 25% is sufficient) to be available for the production of tetramethylene-bis-NN'-ethylene urea with the yield of 84.2%, when the concentration was 21.5 per cent.

**Experiment:** This was followed approximately in the same way as above

### I. Raw materials used and others

(1) Monoethanolamine: imported from abroad; yellowish dark colored; the range of boiling point was  $160^{\circ}\sim 168^{\circ}\text{C}$  (not corrected) by an evaporation test; 95 per cent of distilled fraction existed between  $165^{\circ}$  and  $168^{\circ}\text{C}$  (the value of b. p. shown by a literature is  $170.5^{\circ}\text{C}$ ).  $n_D^{20}$  1.4660 (the value of a literature 1.4539);  $d_4^{20}$  1.020 (the value of a literature 1.018). The concentration was measured by means of the titration by 0.1N hydrochloric acid (factor=1.0489) with the mixed indicator of methyl red and methylene blue, and it was a little less than 98.9 per cent. It is said that the standard method uses methyl purple as an indicator in the titration of a total amine concentration (methyl purple changes its color in the range of pH from 0.1 to 3.2; from yellow to purple).

(2) Preparation method of the mixed indicator: 0.4g methyl red Dissolve in 15.2ml. of 0.10N-NaOH, then add the aqueous solution of 0.2g methylene blue to it up to one liter.

(3) Sulfuric acid for industrial use: specific gravity 1.845 (by azeometer); a colorless, transparent liquid; concentration 96.2 per cent.

(4) Caustic soda for industrial use: flakes; this was presumed as such whose concentration was 90 per cent.

### II Proportion of monoethanolamine and sulfuric acid

It seems to be the most important point that they are added in their equivalent quantities. For example, take sulfuric acid 9.0652g accurately in a weighing bottle by a chemical balance, after pouring it into a messflask of one liter, full with distilled water accurately up to its mark in the ruled temperature. Take the acid into a burette whose inner wall is completely cleaned so far as not to adhere water dropwisely, and titrate monoethanolamine 1.8456g which was taken by balance in weighing bottle and transfused into an Erlenmeyer flask with above mixed indicator of methyl red and methylene blue, then 167.4ml. of sulfuric acid was necessary, for instance, so as for red color to continue more than 30 seconds. Calculation;

$$9.0652\text{g} \times \frac{167.44}{1000} = 1.5179\text{g}$$

$\text{H}_2\text{SO}_4$  equivalent to monoethanolamine

$\text{H}_2\text{SO}_4$  monoethanolamine

equivalent quantity 1.5179  $\times$  2 1.8456

quantity used 207.2 126.0 (2.034 moles)

### On the reaction of $\text{H}_2\text{SO}_4$ and diethanolamine coexisting in monoethanolamine:

upon heating diethanolamine with 70 per cent sulfuric acid at  $160\sim 170^{\circ}\text{C}$ , morpholin  $\text{O} \left\langle \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \right\rangle \text{NH}$  is produced; the latter can be isolated by dehydration on boiling with strong alkali and distillation. Morpholin is a hygroscopic, oily matter which is easily moving, having a similar odor as piperidine, being strong alkaline, whose volatility being increased by ether or water vapors; boiling point  $128^{\circ}\text{C}$  (760mmHg),  $D_4^{20} = 1.0007$ ,  $n_D^{20} = 1.4540$ .

### III Production of ethyleneimine

(1) Beta-aminoethyl acid ester of sulfuric acid: Take sulfuric acid 207.2g and the about half weighted industrial water into a flask of three liter in size, having three mouths, with cooling in an ice water bath and with stirring, then add monoethanolamine 161.1g diluted with the half industrial water through a tap funnel with continuing at below 15°C by a thermometer held at one mouth of the flask (the temperature is not always necessary below 15°C, but sufficient below 50°C, the essential meaning does not exist in the figure 15°C). The weight of the raw material is desirable to keep an exact equivalent quantity as much as possible in order to elevate the yield though it is treated with a rough balance. Since excess water may be allowed, wash out the raw material adhered to the vessel with water into the reaction vessel.

After the addition of amine, on removing the stirrer, join a very fine capillary tube to the flask, attach a thermometer of about 250°C, and set a simple distillatory apparatus involving glass spheres or Raschig rings having a cooler on its upper end, dehydrate the content of the flask in a vacuum of 40mmHg by heating the flask in an oil bath. Increase the temperature rapidly to 185°C, and as soon as it rises to 185°C continue dehydrating for 30 minutes to one hour, then on removing the heating, leave the flask to cool as it is in the oil bath. The temperature of the content becomes higher by several degrees than the temperature of the bath immediately after educing the crystal, but as soon as the reaction approximately completes the temperature of the content becomes to decrease.

**Example of experiment:** with absorbing by a vacuum pump make the content of the flask rapidly increase to about 185°C. If splashes had adhered of the wall inside the reaction flask on the occasion of adding monoethanolamine, it is found that after dehydration those spots have become black on carbonizing. To avoid this it is desirable to wash the wall fully by water

**Table 1.** Dehydration process in the reaction between monoethanolamine and sulfuric acid

bath temp., °C	inner temp., °C	conditions for water to distil	time, minutes
185°	185°	1 drop/sec.	(after educing of the crystal) 5~
"	188°	ditto	ditto
"	185°	water is scarcely distilled any more, when the inner temp. begin to decrease	11~
"	"	water is yet distilled, but in the meantime scarcely being done	15~
"	"	water can not be seen to be distilled, remove the heating,	30~
remove the heating	leave to cool	continue the vacuum alone	up to 60~
85°	95°	remove the vacuum because dehydration has completed, colorless, transparent crystals are seen on the wall	up to 60~

(since the excess water is indifferent for the reaction) or to bathe the upper wall by the content of the flask uniformly before the dehydration. From about the time when water is almost exhausted the temperature of the content goes up over 100°C, and crystals educe instantaneously at about 160°~170°C. It is seen that colorless, transparent and needle-shaped crystals have grown in the end.

#### IV Synthetic process of ethyleneimine from $\beta$ -aminoethyl acid ester of sulfuric acid

**Example of experiment:** when the above content of the flask is cooled to the room temperature the crude ester is weighed with tare,

crude ester	288g
theoretical quantity	287.7g
difference	0.3g

Monothanolamine and  $H_2SO_4$  both can not be distilled by 40mmHg at 185°C; if either is much more than the other, the remainder (or the difference) might become much more than above case. The distilled water does not show alkaline by phenolphthalein.

Add industrial water about 1225ml. and 50% aqueous solution of NaOH 216g to the content of the flask and dissolve the ester with stirring at the room temperature, then a transparent aqueous solution is obtained. Bring in the flask boiling stones made by kneading a glass tube for smooth ebullition without bumping, soak the flask in an oil bath, use a rectifying column packed with Raschig rings. It is very important to choose the rectifying column in this case. For upon contacting ethyleneimine, which had already entered the column again dropped into the flask, with the temperature over 100°C as well as the acid ester which might be a catalyst for polymerization, it results to be polymerized in such a polymerization condition and the yield is thus lowered. It is necessary for some ethyleneimine to reflux at the upper column end by means of the cooling that part by a constant current of water. In the beginning, almost water only comes along at the column upper end, so that wait for some time the concentrated ethyleneimine appears to the end by continuing a complete back flowing. The author made ethyleneimine distill after a complete reflux for 10~20 minutes long at the start. Connect an ordinary cooler to the rectifying column, moreover make an adapter joined to the cooler follow a trap made of a bottle having concentrated caustic soda solution so as to avoid entering the system carbon dioxide or other acidic gases which otherwise polymerizes ethyleneimine and accordingly lowers the yield, and also to hold the atmospheric pressure in the column. The exit of the trap is joined by a long rubber pipe whose another end is inserted deep into the water pipe in which water is flowing in order to make the poisonous gas dissolve into the running water and thus for an operator not to breathe the gas. Cool the receiver of 500ml. capacity attached to the adapter by cold water; when the room temperature is high, ethyleneimine evaporates to a extent that a rubber stopper attached to the receiver is dissolved by the vapor.

Upon dropping a solution of caustic soda from the upper end of the rectifying column so as to avoid the polymerization of ethyleneimine in the column and at the same time to increase the volatility of ethyleneimine from water, the ease of the distillation of ethyleneimine and accordingly the yield is thus made turn to their advantage. According to our experiment, it is effective to exert the reflux sufficiently at the column end in order for ethyleneimine densely to distil as much as possible, and also at the time when ethyleneimine can not distil by all means to make ethyleneimine which would remain only in the column effuse out along with some quantity of water.

**Table 2.** Example of distillation of ethyleneimine from the reacting solution

(heating or) distilling time, (minutes or) hours	bath temp. (inner temp.), °C	distillation velocity, drop/sec.	ethyleneimine, ml.	distilling temp., °C	50 % NaOH dropped from column end, g
0	start to heat the oil bath violently				0
15	130 (75)				0
25	130 (100)	the reflux starts			0
30 (minute)	130 (100)	ethyleneimine starts to distil			50
0.5 (hour)	121	1/4 5	10	62~65 (1)	↓
1.0	120	1/4	22	60~	50+50
1.5	120	1/4	37	63~64 (2)	↓
2.0	123	1/3	51	64~67 (3)	↓
2.5	123	1/4	60	69~70	100+50
3.0	125	1/4	70	71~	↓
3.5	130	1/5~6	75	72~78	150+30
4.0	130	1/5	81	75~83	↓
4.5	113	1/2	105	90~96.5 (4)	180+30
5.0	130	1/2	155	97~	↓
5.5	138	1/2~3	245	97~	↓
6.0	138	—	301	98~	210+14

(1) Distilling temperature is not constant and sways, imine slowly effusing.

(2) Distillation proceeds with a favorable tone.

(3) Reflux water is constant, distillation of imine is regulated by the allowance of heating

(4) In order to make imine in the part of reflux effuse out by lowering the reflux temporarily.

Total NaOH used.....222g (about 5.6 moles; approximately 14 times of ester)

the items:

the first feed.....110g (about 2.8 moles)

one used in dropping from



the upper end of the column.....112g (about 2.8 moles).

As it is shown in a literature that ethyleneimine has a tendency to polymerize merely only by boiling and flowing back without an acidic atmosphere, it appears to be due to its polymerization that the yield of ethyleneimine too often happens to be so low. According to our experience, if it is not to be continued to distil ethyleneimine out keeping pace with the progress of the reaction, the yield is lowered. Therefore, when about 25 per cent of ethyleneimine concentration is needed as a final product, the distilling velocity of imine should be necessary to continue at one drop in 4~5 seconds in the case where the size of the feed is of about 2 moles of raw material, and moreover after about five hours continuation of distillation it appears to be desirable that so as to be exhausted within about 6 hours from the beginning and that in order for 25 per cent of imine to be obtained, ethyleneimine which will yet remain a little in the column should be made to effuse out with water in the end. For the high yield a detailed examination with regard to this point should be carried out. The temperature of distillation is regulated by the distilling velocity and the reflux ratio. Approximately 73g of ethyleneimine should be distilled in this case, hence for the production of 25 per cent ethyleneimine the aqueous solution of imine is presumed to be about 290g and the volume of the solution obtained is considered to be about 300ml. and so on; in this manner the aqueous solution in the receiver is possible to bring to the desired amount.

The yield is measured by the titration of 0.1N hydrochloric acid. The titration is carried out with slow dropping from a burette, and the final point of the titration is one in which the red color continues for 30 seconds. For example; the volume of the aqueous solution of ethyleneimine in the receiver is 351ml. which is weighed to be 343.5g; take 5ml. of the aqueous solution by a whole pipet (the pipet should be drawn up with suction by aspirator and not the mouth, dilute to 100ml. by messflask, take 10ml. from the latter, titrate it by 0.1N HCl (factor=1.0489), use the mixed indicator of methyl red and methylene blue already stated, needing, for example, 23.20 ml. of 0.1N HCl. from this value ethyleneimine obtained is to be 73.7g, the yield 84.2% (calculated from monoethanolamine) and its concentration 21.5%. Calculations:

$$23.20 \times 2 \times 1.0489 \times 0.004306 \times 351 = 73.7\text{g}$$

0.1N-HCl ml.      a multiplier      factor of HCl      from M. W.      volum of ethyleneimine obtained ml.

$$100 \times \frac{73.7}{34.5^*} = 21.5\%$$

(\*aqueous solution, g)      concentration of ethyleneimine

$$100 \times \frac{73.7}{87.6^\dagger} = 84.2\%$$

(†2.034moles of ethyleneimine)      yield in the basis of 2.034moles equivalent of H<sub>2</sub>SO<sub>4</sub>

## V Apparatus

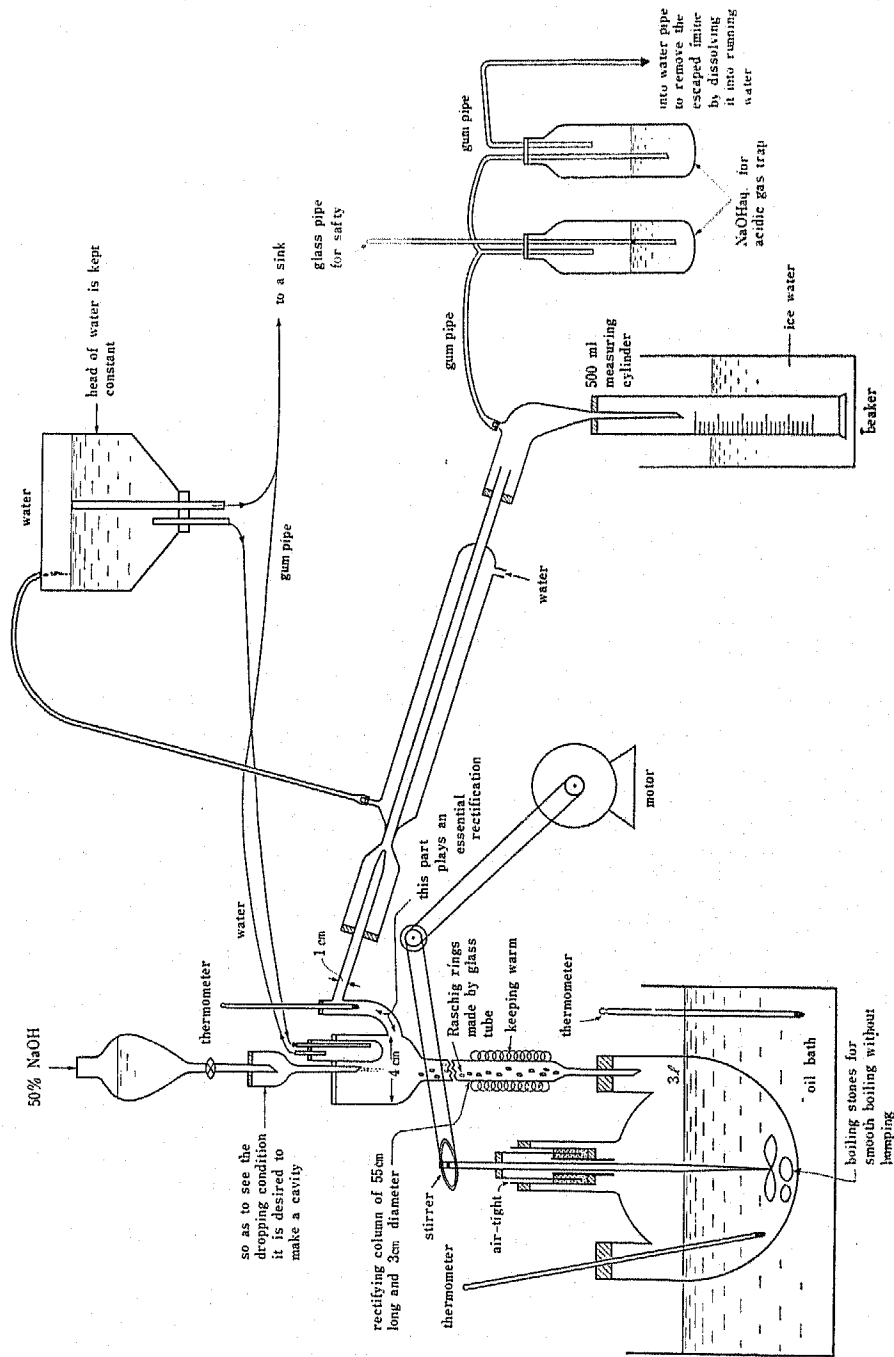


Fig. 1 Apparatus of production of ethyleneimine from  $\beta$ -aminoethyl acid ester of sulfuric acid

## VI Experimental results

raw materials	purities, %	weight	moles	ethylene- imine	yield from monoetha- nolamine	concentra- tion, %
monoethanolamine imported from abroad	a little less than 98.9	126.1	2.034	72.5	84.2	21.5
H <sub>2</sub> SO <sub>4</sub> for industrial use	96.2	207.2	2.034/2			
NaOH for industrial use	some 95	217	ca. 5.4			
monoethanolamine imported from abroad	a little less than 98.9	126.0	2.034	69.5	80.8	98.4
H <sub>2</sub> SO <sub>4</sub> for industrial use	65.21	301.0	2.0/2			
NaOH for industrial use	some 95	335	ca. 8.4			

CONSIDERATION FOR INCREASING THE YIELD OF  
ETHYLENEIMINE

For the high yield and in a case where ethyleneimine concentration is useful even of 20 per cent, it appears to be advisable that on making ethyleneimine distil with as high concentration as possible to the end, and as soon as ethyleneimine does not distil any more it is effused with water in the column by heating its lower part. When the bath temperature arrived at 121°C, ethyleneimine was seen to continue distillation with constant at 53~54°C, under these circumstances it will be seen that the rectifying ability of the column is the most important point for the high yield; to this end the temperature difference between the upper and the lower parts of the column will be desirable to be over 10°C, by doing this it is easily attained that ethyleneimine will distil from the column end at its boiling point.

Upon avoiding for water to mix into the first fraction, after continuing reflux for 10~20 minutes ethyleneimine is made to start for distillation into the cooler at its boiling point. It is thought that in this production of ethyleneimine the size of the experiment, viz., the quantity of the raw materials treated etc. might influence the yield of the product; in the case using the same rectifying apparatus the bath temperature was lowered, for example, to about 107°C depending on the quantity of raw materials.

Even when the Raschig ring are not used, and the column is sufficiently high not to distil water and has a proper slope of temperature, ethyleneimine distils at its boiling point, but the distillation stops faster than used Raschig rings, hence in the former case the yield will decline.

The author endeavors, by increasing the temperature of the lower part

of the column to over 100°C, to avoid for the imine once arrived at the column again to fall into the flask and to contact with the acid ester which may have a property to polymerize the imine, and by regulating the temperature slope of the column and choosing the shape and the size of the Raschig rings, the imine existing in the lower part of the column in the long run to be transferred successively to the upper part. Moreover, it might be useful to make ethyleneimine immediately after produced leave smoothly from the reaction solution without polymerizing by making boiling stones thoroughly effective, since if the imine remains longer in the solution, there would be a lot of chances to polymerize it at all events.

It appears that  $\beta$ -aminoethyl acid ester need not be refined any more; it is most important only to complete the dehydration in the production of the acid ester. It will be seen that in any case the reaction yield is determined by the purities (or the absolute amounts of the objectives) of raw materials and the ability of the rectifying column and approaches to a certain limiting value, and some detailed attention about the operation is indispensable for increasing the yield particularly in this reaction.

#### SUMMARY

The author gives an outline, first, the manufacturing process of the synthesis of tetramethylene-bis-NN'-ethylene urea and each of the four steps, and concludes that the difficulty exists in the reaction between adipic dichlorodiamide, ethyleneimine and caustic soda (the fourth process) peculiarly in the manufacturing of ethyleneimine, hence he states in detail the mechanism in the latter reaction and the reactivity of isocyanates etc. The method used for the manufacturing ethyleneimine in this paper is the one via  $\beta$ -aminoethyl acid ester of sulfuric acid. The author emphasizes that in the synthesis of ethyleneimine the ability of the distillatory column by which ethyleneimine is brought out from the reacting solution is the most important point among other things, and he states a detailed procedure for the synthesis of ethyleneimine thoroughly.

#### REFERENCES

- 1) R. Adams, "Organic Reactions" vol. III (1946) p. 268
- 2) C.R. Hauser and W.B. Renfrow Jr., J. Amer. Chem. Soc., **59** (1937) 121
- 3) H. Gilman, "Organic Chemistry, an advanced treatise", II, 1874
- 4) F.I.A.T. Final report, No. 960, October 10, 1946