The Dechlorination of Polychlorinated Biphenyls with Alkali in 1,3-Dimethyl-2-Imidazolidinone

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1. Introduction

Among numerous organohalogen compounds, which are found in our environment, polychlorinated biphenyls (i.e. PCB) especially are known as stable and toxic.
The affinity of polar aprotic solvents for the dechlorination of PCB with alkali were surveyed, including 1,3-dimethyl-2-imidazolidinon (i,e. DMI) . DMI was found to be the best solvent for this process at rather elevated temperature (200°C-210°C) and atmospheric pressure. [1)-5) etc.]
PCB, from 10 ppm in transformer oil (i.e. TFO) to 100% Kanechlor 500, were dechlorinated to lower PCB concentration than 1 ppb, detected by high resolution Gas Chromatgraphy Mass Spectrometry (i.e. HRGC/MS) .
This process is carried out in closed system safely.

2. Experimental

(1) Apparatus

The appratus shown in Figure 1. was used in the experiments. It consists of a four-necked flask, a stirrer, an oil-bath and a thermometer.

(2) Material

The chemical composition of Kanechlor 500 is listed in Table 1.

Transformer oil (i.e. TFO) has been obtained from Taniguchi Oil Co. and the properties are listed in Table 2. DMI was from Mitsui Toatsu Chemical Co.

(3) Typical experimental procedure

The following experiments were performed.

(a) Dechlorination of 100% PCB (Kanechlor 500)
(b) Dechlorination of PCB-TFO mixture (70% PCB/30% TFO)
(c) Dechlorination of low concentration PCB in TFO (40 ppm-80 ppm)

A hundred grammes of DMI solution, which contains 1 gram of 100% PCB (Kanechlor 500) are poured into the four-necked flask which has the volume of 200 ml or 500 ml. Powdered sodium hydroxide are mixed in the DMI solution as to be 19,000 ppm. The temperature in the system was kept at 200 °C for 2 hours. Then, ten ml of the reaction mixture are taken for analysis. The temperature of the reaction vessel has been kept at 200 °C for 2 hours. Afterwards, ten ml is accumulated for analysis after the reaction finished.
The concentrations of PCB were measured by means of Gas Chromatography Mass Sepctrometry (i.e. GC-MS) . High resolution GC-MS measurements were performed by Toray Research Centre (Kamakura) .
The quantitative analysis of sodium chloride in the reaction products was determined by titration.

3. Results and Discussion

(1) Dechlorination of 100 % PCB (Kanechlor 500)
The results on series of experiments with 100 % PCB in DMI solution (10,000 ppm or 100,000 ppm) are shown in Figure 2. chlorine atoms in PCB (Kanechlor 500) were completely removed. PCB were treated with alkali (powdered sodium hydroxide, potassium hydroxide or sodium alcoholate) for 2 hours to 6 hours at 200 °C (amount Cl was less than 1 ppb after this treatment) .
Most of the chlorine was removed within one hour reaction time. The PCB concentration was less than 1 ppb after 6 hours.
Diethylen glycol (DEG) and triethylene glycol dimethyl ether (TEGDME) scarcely promoted the reaction in this case. DMI was determined by titration. It could be seen chlorine atoms in PCB were almost removed. No organohalogen compounds were detected after this treatment. A more effective dechlorination was achieved when accelerating agents, such as quinoline were added. Quinoline can be effective agent.

(2) Dechlorination of PCB-TFO mixture (70 % PCB/30 % TFO)
The expriments on PCB-TFO mixture (70 % PCB-30 % TFO) were performed to investigate the interaction of TFO in the dechlorination. The results are shown in Table 3. The typical PCB concentration after this treatment resulted 5 ppb in the run for 70,000 ppm PCB mixture and N.D. (less than 1 ppb) in the run for 7,000 ppm PCB mixture.

(3) Dechlorination of low concentration PCB in TFO (40 ppm-80 ppm)
The solutions, which contained 40 ppm or 80 ppm PCB in TFO, were treated by this process for the dechlorination. The results are shown in Table 4. It shows that at the lower temperature as of 155°C the dechlorination reaction proceeded slightly at the end, and also in the lower alkali concentration as of 1,500 ppm.
Alkali at higher concentration, (such as 13,000 ppm) , more than solubility promoted the reaction significantly at 200°C, when the DMI ratio (DMI/TFO) was 1 or 2. The PCB concentration resulted 7.4 ppb or N.D. (less than 1 ppb) after the treatment.

(4) Dechlorination by recycled DMI
The experiments on the recycled DMI were performed to investigate the effect of the reaction products of the treatment. The results are shown in Table 5. Especially, the PCB concentration in the DMI recycled by means of the centrifugal filtration was 7.2 ppb after the treatment. It shows that the reaction products scarcely interfered the dechlorination of PCB. The PCB concentrations in the DMI recycled by means of PCB distillation were between N.D. (less than 1 ppb) and 7.4 ppb after the treatments. It is estimated that the DMI recycled by means of the distillation is equivalent to the fresh DMI in the reaction since the products do not interfere at all.

The reaction temperature has to be above 190 °C, otherwise the dechlorination was not complete (several hundreds ppb of PCB left after treatment) . The molar ratio alkali to chlorine atoms of PCB (Alkali/Cl) , are preferable to keep more than 300 (mol/mol) times for (3) (i.e. 40 ppm-80 ppm in TFO) , and more than 3 times for (1) (i.e. 100 % PCB) and for (2) (i.e. 70 % PCB/30 % PCB) . The higher ratio of alkali to Cl atoms gave better results.

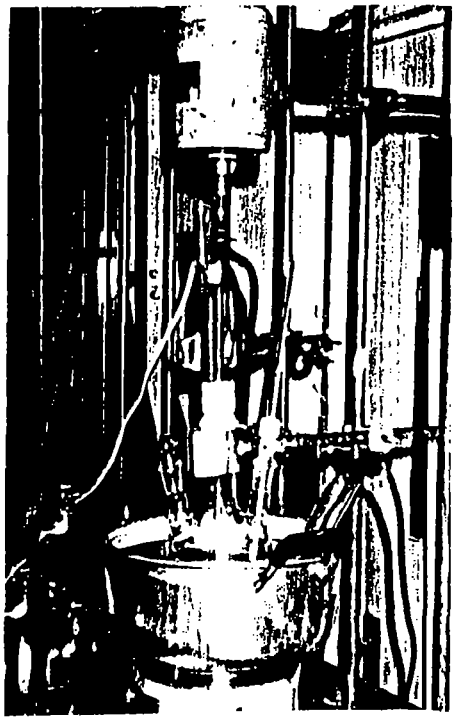

Figure 1. EXPERIMENTAL APPARATUS

Table 1. CHEMICAL COMPOSITION OF Kanechlor 500 (10,000 ppm)

(p p b)

	1 (ppb)	2 (ppb)
MonoCBs	180	130
DiCBs	40,000	37,000
TriCBs	170,000	150,000
TetraCBs	2,100,000	1,900,000
PentaCBs	4,500,000	4,400,000
HexaCBs	3,400,000	3,200,000
HeptaCBs	220,000	140,000
OctaCBs	4,400	2,200
NonaCBs	300	100
DecaCBs	200	90
Total PCBs	10,000,000	9,900,000

Table2. Transformer Oil (TFO) Properties

	Condition	Properties
(1) Color		ASTML 0.5
(2) Corrosion	140℃ 19h	2n
(3) Breakdown voltage		>50KV
(4) Vapor		0.20wt%
(5) Flashing point		136℃
(6) Acid value		0.3 mg KOH/g
(7) Pour point		< 50.0℃
(8) Acidity Alkalinity		Neutral
(9) Density	15℃	0.8889g/cm³
(10) Resistivity	80℃	1.5×10^{13} ohm·cm
(11) Kinematic viscosity	100℃	2.094 cSt

Table 3. EXPERIMENTAL RESULTS (70%PCB/30%TFO)

	Experimental Condition *1						Results
No.	Solvent	Alkali	Alkali ratio (Alkali /Cl atom)	Alkali concentration (ppm)	Time (h)	Initial PCB concentration (ppm)	PCB concentration after treatment (ppb)
1	DMI	NaOH	3	130,000	6	70,000 (TFO 30%)	32
2	DMI	KOH	3	180,000	6	70,000 (TFO 30%)	36
3	DMI	NaOH	6	260,000	6	70,000 (TFO 30%)	20
4	DMI	KOH	6	360,000	6	70,000 (TFO 30%)	22
5	DMI	NaOH	9	390,000	6	70,000 (TFO 30%)	11
6	DMI	KOH	9	540,000	6	70,000 (TFO 30%)	5
7	Sulfolane	NaOH	3	130,000	6	70,000 (TFO 30%) (210℃)	740,000
8	DMI	KOH	3	18,000	6	7,000 (TFO 0.3%)	N. D. *2

*1 Reaction at 200℃
*2 N. D. : Not detected (less than 1ppb)

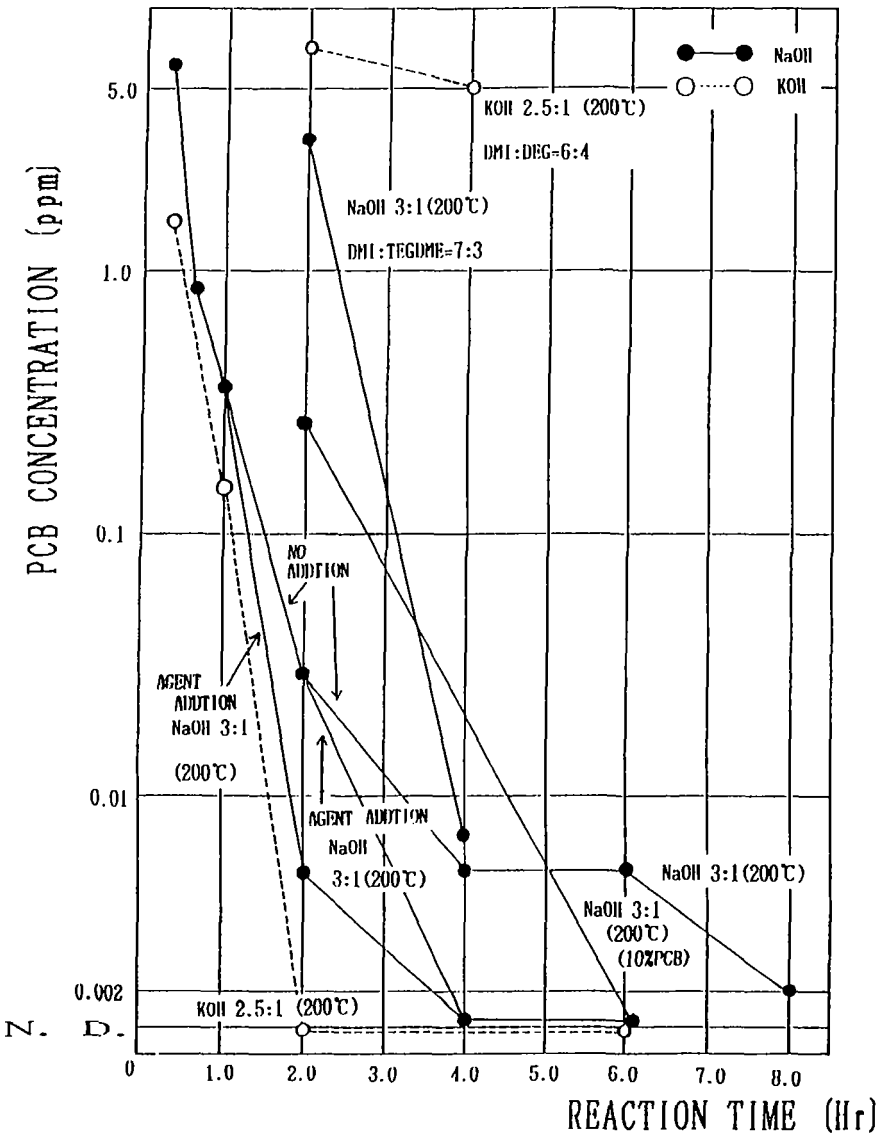

Figure 2. EXPERIMENTAL RESULTS (KANECHLOR 500) (1%PCB)

Table 4. EXPERIMENTAL RESULTS (LOW CONCENTRATION PCB IN TFO)

No	Experimental Condition						Results
	DMI ratio (DMI /TFO)	Alkali ratio (Alkali /Cl atoms)	Alkali concentration (ppm)	Temperature (℃)	Time (h)	Initial PCB concentration (ppb)	PCB concentration after treatment (ppb)
1	1/2	NaOH 600	60,000	155	4	40,000 (40ppm)	7,300
2	1/2	C_2H_5ONa 200	20,000	155	2	40,000 (40ppm)	1,200
3	1/1	NaOH 30	1,500	200	6	80,000 (80ppm)	3,000
4	2/1	NaOH 500	13,000	200	6	80,000 (80ppm)	7.4
5	2/1	KOH 500	18,000	200	6	80,000 (80ppm)	N.D.*1
6	1/1	NaOH 6,000	160,000	200	6	80,000 (80ppm)	N.D.*1

*1 N. D. : Not detected (less than 1 ppb)

Table 5. EXPERIMENTAL RESULTS (RECYCLED DMI)

No	Experimental Condition *1						Results
	Recovery Method	Initial PCB concentration (ppm)	DMI ratio (DMI /TFO)	Alkali ratio (Alkali /Cl atoms)	Alkali concentration (ppm)	Time (h)	PCB concentration after treatment (ppb)
1	Centrifugal Filtration	80 TFO	3	NaOH 1,500	26,000	6	7.2
2	Rotary Evaporation	70,000 DMI	30 (3% TFO)	NaOH 9	390,000	6	1.6
3	Rotary Evaporation	80 TFO	2	KOH 500	18,000	6	N.D. *2
4	Distillation (Claisen)	80 TFO	2	NaOH 500	13,000	6	7.4

*1 Reaction at 200℃

*2 N.D. : Not detected (less than 1 ppb)

4. Conclusion

The following conclusions are able to say from the experiments.

(1) The dechlorination of PCB increased with the reaction time and finished within 6 hours in DMI with alkali at 200°C. The PCB concentration of 100,000 ppm became N.D. (less than 1 ppb) after this treatment. The reaction temperature should be above 200°C.
(2) The DMI is the best solvent the dechlorination (compared to sulforan) .
(3) Alkali concentrations less than 2,000 ppm scarcely promoted the dechlorination of PCB.
(4) The accelerating agents such as quinoline promote more rapidly the reaction.
(5) The DMI solution of 70,000 ppm PCB and 30,000 ppm TFO (i.e. PCB-TFO mixture) was dechlorinated to 5 ppb. In this case, the dechlorination of PCB was somewhat interfered. The DMI solution of 7,000 ppm PCB and 3,000 ppm TFO was dechlorinated to N.D. (less than 1 ppb) .
(6) All Cl atoms in PCB are removed and can be isolated as sodium chloride or potassium chloride.
(7) The DMI recycled by means of centrifugal filtration dechlorinated to 7.2 ppb. It proved that the reaction products after the treatment scarcely interfered the dechlorination of PCB.

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