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Perchlorination Reaction Applied to the Rapid Determination of PCBs

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Quantitative determination, as well as qualitative analysis, is required in order to investigate the global dynamics of PCBs in living organisms and the environment. Thus, development and establishment of a practical method by which PCBs can be determined accurately and rapidly has been an objective.

SILBERRAD (1922) introduced the BMC reagent ($SO_2Cl_2 - S_2Cl_2 - AlCl_3$) for preparation of polychloro-derivatives of benzene. HUTZINGER (1972) investigated the reagent for the analysis of PCBs and some other chlorinated aromatic hydrocarbons and reported it to be most effective and convenient. NOSE & AKIYOSHI (1973) used the reagent for the quantitative determination of PCBs at atmospheric pressure. The method, however, did not give excellent results.

Our method is based on a discovery of the phenomenon that the amount of decachlorobiphenyl (DeCB) synthesized reaches a plateau after a certain time and moreover a definite amount of DeCB is synthesized from a certain amount of PCBs despite its weight-percent of chlorine in this reaction, which is expressed in the following equation.

a μg (PCBs : KC-300, 400, 500, 600) $\longrightarrow$ b μg (DeCB)
b/a = 1.1 , Reaction temperature and time : 64–67°C , 45 min
or 59–62°C , 1.0 h

Consequently, the concentration of PCBs in a sample can be easily calculated from the DeCB value, and determined with an error of less than 10%.

MATERIALS AND METHODS

Chemicals : Kaneclor-300, 400, 500, and 600, commercial names of PCBs sold and used in Japan, were purchased from Gasukurokogyo (Tokyo, Japan). DeCB standard and sulfurylchloride containing 1% sulfur monochloride were obtained from Wako-Pure-Chemical (Tokyo, Japan), and the brown ampoule containing the chlorinating reagent (5 mL) was opened just prior to use. Anhydrous $CaSO_4$ (8 mesh) was purchased from Hammond (Ohio, U.S.A.).

Perchlorination reaction : The apparatus, procedures of the experiment, and the preparation of GLC sample are shown in Figure 1 and Table 1, respectively. Distilled water was added to hydrolyze the residual reagents after the reaction was completed.

Gas chromatography : DeCB was analyzed by a gas chromatograph equipped with the electron-capture detector (ECD). A glass column (3 mm x 1 m) packed with 1% OV-1 or DEGS-H_3PO_4 (2-0.5%) on Chromosorb WAW was used. Gas flow rate of high purity nitrogen was controlled for DeCB to be eluted in ca. 10 min. A.C. voltage in the ECD was primarily 30 V.

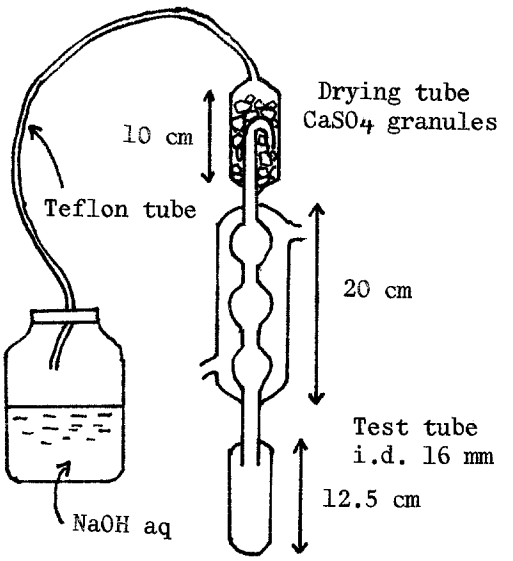

Figure 1 Modification of the reaction apparatus presented by NOSE & AKIYOSHI (1973).

Table 1. Procedures of DeCB synthesis and preparation of GLC sample

1) Add cleaned up solution (1.0 mL) of hexane containing PCBs into the test tube
2) Evaporate the solvent in a drying oven maintained at 70°C for about 1.5 h and then all residual hexane must be removed gently in an aluminium block heater preheated at ca. 65°C
3) Add SO_2Cl_2 (1.0 mL) containing 1% S_2Cl_2 into the tube from the ampoule
4) Add $AlCl_3$ (40 to 100 mg)
5) Fit the test tube with a reflux condenser equipped with a drying tube and heat at the optimum reaction condition in a glycerin bath
6) After chlorination, the residual solution will be gently hydrolysed by the addition of distilled water (5 mL) and intermittent mixing
7) Add hexane (5 or 10 mL) into the tube, and extract DeCB by shaking vigorously
8) Separate the hexane layer and wash it with 1N-NaOH (5 mL)
9) Separate the upper layer and dry by means of Na_2SO_4 (ca. 1g) addition

RESULTS

An early stage of perchlorination reaction

Some intermediate compounds were detected as peaks of shorter retention time as compared to DeCB. Three peaks were recognized before DeCB eluted, as shown in Figure 2.

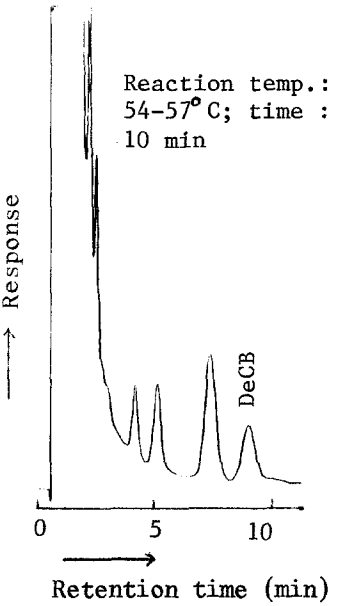

Figure 2. Intermediate products produced in the reaction

Time courses of DeCB synthesis at some reaction temperatures

The amounts of DeCB were plotted with times in two cases of reaction temperature at ca. 45°C and 55°C (Figure 3). In the former, it is uncertain whether DeCB values are increased with the length of reaction time or not. In the latter case, they are increased gradually with the period, but direct proportion between DeCB values and reaction periods is not observed.

The time courses of DeCB synthesis at the further high temperature, i.e. ca. 60°C and 65°C are shown in Figure 4. The amount of DeCB synthesyzed at ca. 60°C reaches a plateau in about 50 min. On the other hand, time course curve of early stages at ca. 65°C is slightly steeper than at ca. 60°C, and then the value

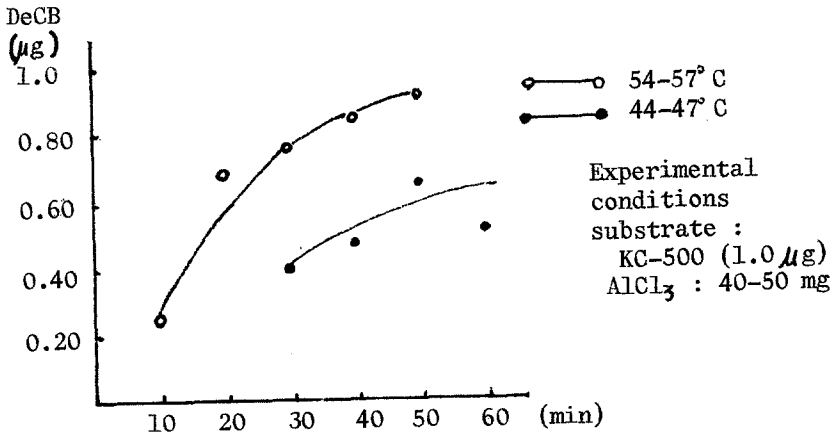

Figure 3 Effect of low reaction temperature on the pattern of DeCB synthesis

similarly reaches a plateau of the same level in about 40 min. In this case, its value was 1.15 g per 1.0 g of substrate.

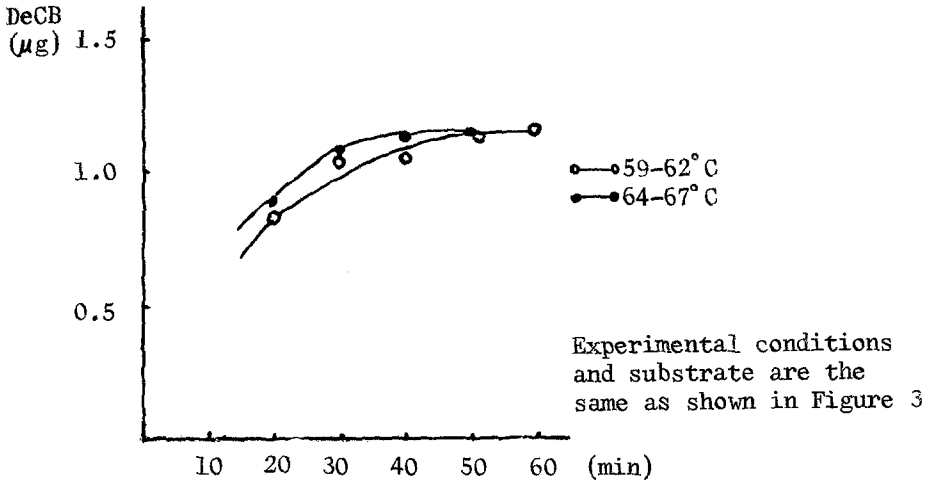

Figure 4 Optimum temperatures of DeCB synthesis and their time cources

Relationship between substrate amount and DeCB value

DeCB amounts were determined in the range of substrate KC-500 from 0.10 to 10 μg (Figure 5). Direct proportion is observed between amounts of substrate and those of DeCB. In other words, the following equation was concluded to exist in this reaction.

a μg (KC-500) ⟶ b μg : b/a ≈ 1.15

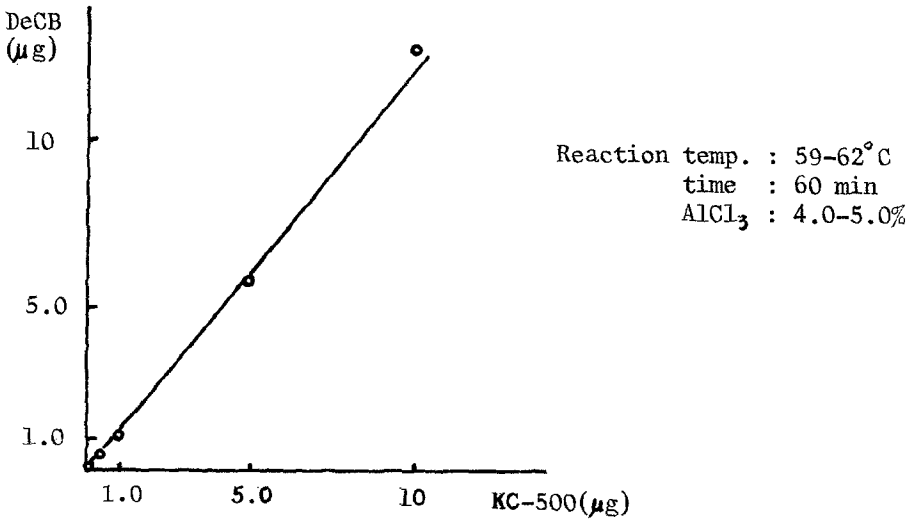

Figure 5 Relationship between the amounts of substrate and those of synthesized DeCB

Relation between various commercial PCBs and DeCB values

The difference of DeCB values were investigated in some cases of commercial PCBs containing various chlorine contents (Table 2). The amounts synthesized from various PCBs are too close, and their range is very narrow, i.e. 1.07-1.16 μg per 1.0 μg of various substate. Consequently, the equation can be applied also to PCBs mixture of various chlorine contents.

Table 2. Commercial PCB mixtures of various chlorine contents and their DeCB values

Commercial PCBs	Formula (approx.)	Substrate (μg)	DeCB (μg)
KC-300	$C_{12}H_7Cl_3$	1.0	1.11
KC-400	$C_{12}H_6Cl_4$	1.0	1.16
KC-500	$C_{12}H_5Cl_5$	1.0	1.07
KC-600	$C_{12}H_4Cl_6$	1.0	1.09

Reaction conditions : Temperature ; 64-67° C, Time ; 40 min
Experimental conditions are the same as given in Figure 3

Effect of the amounts of $AlCl_3$ upon DeCB synthesis

The appropriate amounts of $AlCl_3$ required in the reaction were investigated. The DeCB values didn't reach maximum level with less than 20 mg of $AlCl_3$, but the expected constant values were obtained with more than 33 mg (Table 3).

Table 3. Relationship between various $AlCl_3$ concentrations in the reaction mixture and DeCB values

Added $AlCl_3$ (mg)	DeCB (μg)	Experimental conditions
10	0.83	Substrate : KC-500 (1.0 μg)
19	0.85	Room temp. : 18-19°C
33	1.06	Relative humidity : 57%
40 – 50	1.06	Reaction condition : 64-67°C, 45 min
69	1.06	
40 – 50	1.05	Relative humidity : 65%
71	1.03	Other conditions are the same as
79	1.02	described above
88	1.06	
98	1.02	

DISCUSSION

Hexane must be completely removed before the reagent of perchlorination is added into the test tube. If a trace of the sol-

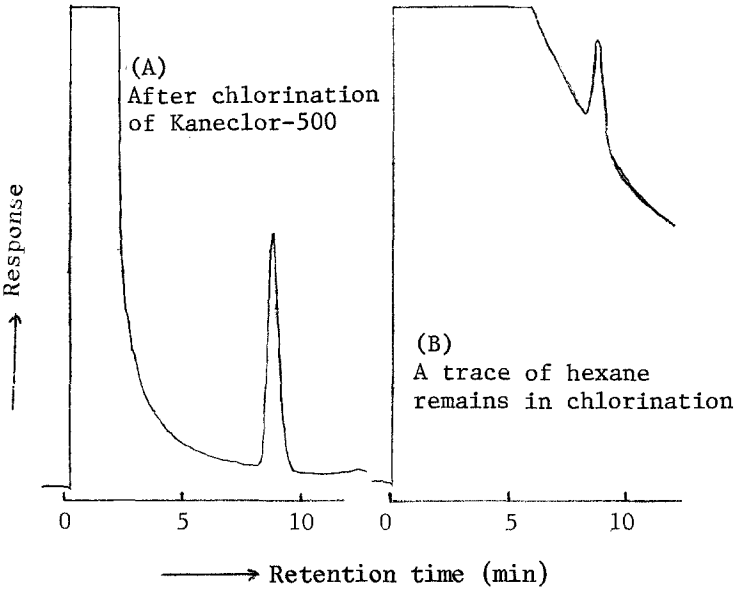

Figure 6. GC/EC chromatogram of chlorinated sample.

vent remains, a large peak will be eluted in GLC trace immediately after a sample injection, as shown in Figure 6. Consequently, the sensitivity of ECD for DeCB declines considerably. Therefore, the test tube should be remained open for a while after complete removal of the solvent. Room temperature of the laboratory being relatively low in winter, test tubes were left open for ca. 15 min.

More than 40 mg of $AlCl_3$ should be usually added into a test tube containing one mL of the reagent. The surfaces of the $AlCl_3$ granules absorb moisture during weighing and gradually lose its potency. But, it seems that contamination of $AlCl_3$ hydrate does not inhibit DeCB synthesis. Therefore, rapid operation to reduse water absorption by $AlCl_3$ as much as possible may be not essential.

The moisture in the apparatus seems also to be unimportant, because the vapour of SO_2Cl_2 catches moisture and then is gradually hydrolyzed into hydrochloric and hydrosulfuric acids. Consequently, a vessel containing a dessicant, i.e. $CaSO_4$ granules, may not be essential for the apparatus (Figure 1).

The record of ECD-GC will apparently give unexpected high values of DeCB if the reaction should be continued beyond the appropriate reaction period until a solution of the reagent scarcely remains in a reaction tube.

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