Thermal Stability of Phthalic Esters

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ABSTRACT

Phthalic esters, as typical plasticizers for vinyl plastics, were thermally decomposed by a flow reactor system and their decomposition products were analyzed in detail. The thermal decomposition products were olefin, alcohol, hydrogen phthalate, benzoates with alkyl groups corresponding to these of the original phthalate esters and phthalic anhydride. We found from the main thermal decomposotion products—olefin, alcohol and hydrogen phthalate—that phthalic esters were thermally decomposed through *cis*-elimination in the same way as in the general case for esters. In the presence of polyvinyl chloride (PVC), hydrochlorinated products were identified in the decomposition products. A good relationship was found between the amount of chloroalkanes produced and the reaction temperature. The *cis*-elimination reaction of phthalic esters was found to be promoted by PVC.

INTRODUCTION

Phthalic esters are used in large quantities as plasticizers of polyvinyl chloride (PVC), the waste from which has become an environmental pollutant (1). Although phthalic esters are treated at ca. 200 C in the molding process of PVC (2), the reactivity of phthalic esters in the presence of PVC at relatively high temperatures has not been clarified as yet. Gas chromatography (GC) analyses indicate that phthalic esters permeate the whole living environment with pollution problems in drinking water and foods (3-5). Few reports on the analysis of the thermal decomposition products of phthalic esters have been published (6). Their thermal characteristics, therefore, are not well known as yet (7).

Thermal decomposition of the typical phthalic esters was carried out at temperatures ranging from PVC molding temperature (150-200 C) to the combustion temperature (400 C or higher) of the waste, and the heat stability was investigated from the relationship between the reaction temperature and the composition of the decomposition product.

EXPERIMENTAL

Sample and Reagent

The commercial products of dibutyl phthalate (DBP), dioctyl phthalate (DOP) and bis(2-ethylhexyl) phthalate (BEHP) were used for the experiment, whereas dihexyl phthalate (DHP) and didecyl phthalate (DDP) were synthesized from the alcohols (1-hexanol and 1-decanol, respectively) and phthalic anhydride, according to the usual procedure (8). The products were purified by reduced pressure distillation (b.p. of dihexyl phthalate is 230 C/6 mmHg, and b.p. of didecyl phthalate is 258 C/1.5 mmHg). The commercial standard reagents were used to provide the calibration curves of GC except for the alkyl hydrogen phthalates. They were produced by reaction of the alcohols having the appropriate chain length with phthalic anhydride according to the usual procedure (9), and the synthesized products were esterified by diazomethane (10) and purified by reduced pressure distillation (b.p. as follows: methyl butyl phthalate, 156 C/7 mmHg; methyl hexyl phthalate, 170 C/8 mmHg; methyl octyl phthalate, 189 C/4 mmHg; methyl 2-ethylhexyl phthalate, 187 C/8 mmHg; and methyl decyl phthalate, 189 C/4 mmHg).

Analytical Apparatus

The apparatus used for identifying the synthesized samples and for separating and determining the thermal decomposition products are as follows: nuclear magnetic resonance (NMR) spectroscope, Joel FX-100 (^{1}H-NMR and ^{13}C-NMR); gas chromatograph-mass spectrometer (GC-MS), Shimadzu LKB 9000 and OKITAC 4300C; high-mass spectrometer, Hitachi MRU-7M+HITAC 10 II; infrared (IR) spectroscope, Shimadzu IR-420; and gas chromatograph (GC), Shimadzu GC-4BPT or GC-4BPF+chromatopak C-R1A (detector: thermal conductivity or H_2-flame ionization (FID) type).

Thermal Decomposition Procedure and Analytical Method

The thermal decomposition of phthalic esters was carried out in a flow reactor system or a static system (if PVC was present). The schematic diagram of the flow reactor system is shown in Figure 1. The reactor is made of a quartz tube (12 mm i.d. and 410 mm long), which is of double-pipe construction to provide uniform temperature distribution. A sample is continuously fed at a constant rate to the top of the reactor from the reservoir through the high-pressure micropump (Seishin Seiyaku Co. Model PSD 2.5w) while carrier gas (nitrogen) also is fed continuously to the top through the gas flow controller from the cylinder. The top of feed pipe is equipped with a spray nozzle. The reaction tube was heated up to the specified temperature by the heating furnace and kept in a range of ±1 C. The mean temperature was calculated from the vertical distribution of temperature in the reactor by Ohtake et al.'s method (11) to obtain the residence time (12). The temperature of thermal decomposition was measured by an alumel-chromel thermocouple inserted into the center of the reactor.

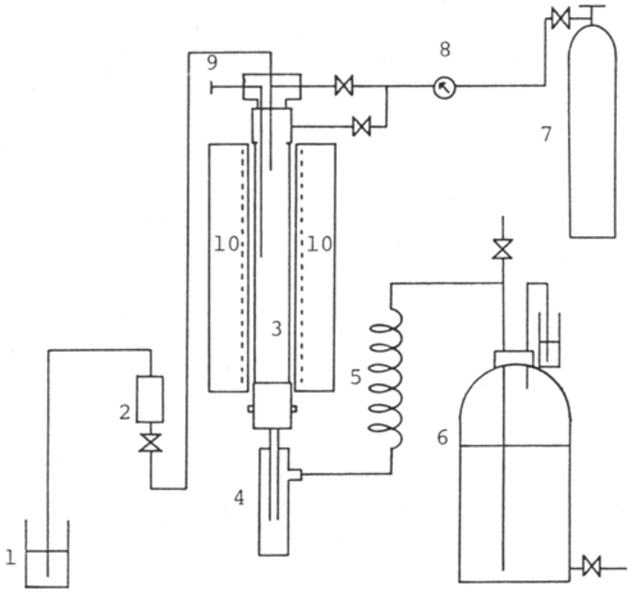

FIG. 1. Flow sheet of experimental apparatus: 1. sample reservoir; 2. high-pressure micropump; 3. reactor; 4. receiver; 5. condenser; 6. gas holder; 7. N_2 cylinder; 8. gas flow controller; 9. alumel-chromel thermocouple; 10. heating furnace.

The sample was thermally decomposed in a few seconds as it passed through the reactor. The decomposition products and the unreacted substance were recovered in the reservoir beneath the reactor, while the carrier gas and the gaseous products were collected through the condenser in the gas holder filled with salt water. The gaseous products were sampled by syringe directly from the gas holder to analyze by GC (Shimadzu GC 4BPT, thermal conductive type detector, column: Porapac Q 80-100 mesh, 3 mm i.d. and 2 m long). The liquid-solids products collected in the reservoir were pretreated with diazomethane and the internal standard was added. The products was taken up with 5-8 mL of acetone to which more acetone was added to make 10 mL of solution. A specific volume of the solution was analyzed by GC (Shimadzu GC-4BPF, H_2-FID, column: 2% silicone OV-17 on Chromosorb WAW DMCS 60-80 mesh, 3 mm i.d. and 2 m long). For qualitative analysis, ca. 20 g of the products obtained by thermal decomposition of phthalic esters at 400 C for 4.2 seconds was used. The components were identified by GC-MS, and by ^{1}H-NMR, ^{13}C-NMR, high MS and IR after isolation.

RESULTS AND DISCUSSION

Analysis of Thermal Decomposition Products

Figures 2 and 3 show the GC analytical results of the thermal decomposition products obtained from bis(2-ethylhexyl) phthalate as representative of phthalic esters in the flow-reactor system.

In Figure 2, each component was identified by comparing with the residence time of a standard gas. The gaseous products increased as the reaction temperature was raised. The gaseous products obtained by the thermal decomposition of every phthalic ester were not determined.

Figure 3 shows the analytical result of the liquid-solids fraction. Because components of low heat stability, e.g., phthalic acid and 2-ethylhexyl hydrogen phthalate as obtained in the thermal decomposition products, were converted to methylesters by diazomethane treatment, analyzing the thermal decomposition products was possible.

Relationship Between Reaction Temperature and Decomposition Product Composition

Phthalic esters with alkyl side chains ranging from butyl to decyl were thermally decomposed to investigate the relationship between the reaction temperature and the composition of decomposition product. The analytical results of the decomposition of the samples are listed in Tables I-V.

Main thermal decomposition products were identified by instrumental analysis, e.g., NMR, IR and high-MS. Olefins (1-butene, 1-hexene, 1-octene, 2-ethyl-1-hexene and 1-decene), alcohols (1-butanol, 1-hexanol, 1-octanol, 2-ethyl-1-hexanol and 1-decanol) and hydrogen phthalates (butyl-, hexyl-, octyl-, 2-ethylhexyl- and decyl-hydrogen phthalates),

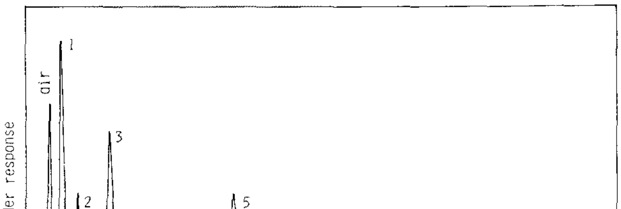

FIG. 2. Gas chromatogram of gaseous products from the thermal decomposition of bis(2-ethylhexyl) phthalate. Apparatus: Shimadzu GC-4BPT packing, Porapac Q 80-100 mesh column (length 2 m, i.d. 3 mm); He flow rate, 30 mL/min; column temperature, 50-200 C; programing rate, 5 C/min. Thermal decomposition conditions: reaction temperature, 430 C; residence time, 4.2 sec dilution ratio (by mol), carrier gas, N_2/sample = 20. Peak: 1. methane; 2. carbon dioxide; 3. ethane; 4. unknown; 5. propane; 6. butane; 7. pentane.

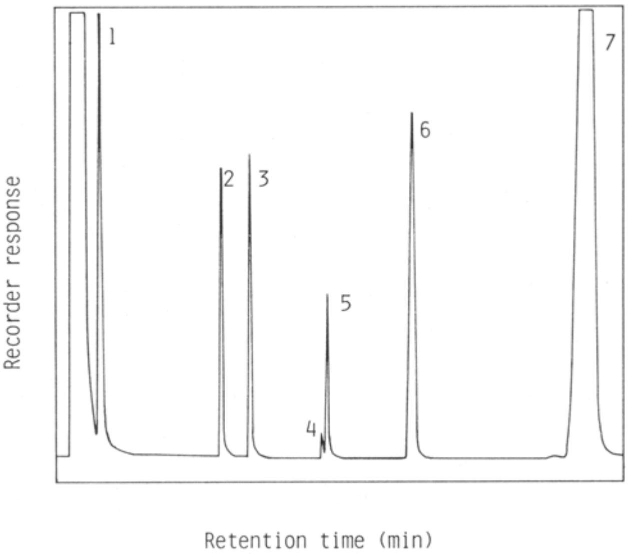

FIG. 3. Gas chromatogram of the liquid-solids products from the thermal decomposition of bis(2-ethylhexyl) phthalate. Apparatus: Shimadzu GC-4BPF packing, silicone XE-60 10% on Chromosorb WAW DMCS 60-80 mesh column (length 2 m, i.d. 3 mm); N_2 flow rate, 30 mL/min; column temperature, 50-250 C; programing rate, 15 C/min. Thermal decomposition conditions: reaction temperature, 430 C; residence time, 4.2 sec; dilution rate (by mol), carrier gas, N_2/sample = 20. Peak: 1. 2-ethyl-1-hexene[6]; 2. 2-ethyl-1-hexanol; 3. standard (ethyl benzoate); 4. dimethyl phthalate (methyl ester for phthalic acid); 5. phthalic anhydride; 6. methyl 2-ethylhexyl phthalate(methyl ester for 2-ethylhexyl hydrogen phthalate); 7. unreacted bis(2-ethylhexyl) phthalate.

TABLE I

Effect of Reaction Temperature on the Thermal Decomposition of Dibutyl Phthalate[a,b]

	Composition of decomposition products, wt %, at							
Component	250 C	300 C	350 C	375 C	400 C	425 C	450 C	475 C
1-Butene	–	–	0.5	1.5	3.5	8.5	16.0	8.4
1-Butanol	–	–	–	2.5	3.0	13.6	16.0	15.3
Phthalic anhydride	–	0.9	2.5	10.0	22.5	41.0	47.9	47.4
Butyl benzoate	–	–	–	0.3	0.5	0.6	1.1	0.6
Methyl butyl phthalate	–	–	–	0.3	0.5	2.5	5.4	–
Dibutyl phthalate	100	99.1	97.0	85.4	70.0	33.8	13.6	–

[a] Sample feed rate; 0.2 mL/min; residence time; 9.7 sec.

[b] Packed column reactor.

corresponding to the side-chain structures and phthalic anhydride.

Extremely small quantity components, e.g., aldehyde, phthalic acid (in the quartz-tube reactor) and benzoate (in the packed-column reactor) were isolated and determined. *cis*-Elimination (13) took place in the thermal decomposition reaction of phthalic esters in the same way as in that of the general fatty acid esters.

The relationship between the thermal decomposition products and the reaction temperature of bis(2-ethylhexyl) phthalate as representative of the phthalic esters is explained in Table III. It began thermally decomposing at 250 C, producing phthalic anhydride, which was detected by GC. The reaction made rapid progress at ca. 380 C, so that the thermal decomposition products (2-ethyl-1-hexene, 2-ethyl-1-hexanol and phthalic anhydride) were produced

TABLE II

Effect of Reaction Temperature on the Thermal Decomposition of Dihexyl Phthalate[a]

Component	Composition of decomposition products, wt %, at									
	200 C	250 C	300 C	340 C	350 C	360 C	380 C	400 C	450 C	500 C
1-Hexene	–	–	0.7	1.4	2.5	2.4	3.7	8.1	36.9	39.8
Hexanal	–	–	–	–	0.3	–	0.1	0.2	0.6	1.2
1-Hexanol	–	–	0.1	0.1	0.2	0.1	0.6	2.0	23.7	30.2
Phthalic anhydride	–	–	–	–	0.1	–	–	1.0	14.9	25.8
Dimethyl phthalate	–	–	0.1	–	0.3	–	–	0.3	1.3	0.9
Methyl hexyl phthalate	0.1	0.2	0.4	0.6	1.4	2.0	4.5	6.4	7.5	0.8
Dihexyl phthalate	99.8	99.7	99.9	99.3	94.4	95.6	91.4	81.9	19.6	1.4

[a] Dilution ratio (by mol); carrier gas, N_2/sample = 20; residence time, 4.2 sec.

TABLE III

Effect of Reaction Temperature on the Thermal Decomposition of Bis(2-ethylhexyl) Phthalate[a]

Component	Composition of decomposition products, wt %, at									
	250 C	280 C	300 C	360 C	380 C	400 C	420 C	450 C	480 C	500 C
2-Ethyl-1-hexene	0.1	0.1	0.2	1.5	3.3	8.9	19.5	41.9	51.3	52.0
2-Ethylhexanal	0.4	0.3	0.6	0.7	0.9	0.3	0.2	0.1	0.2	0.1
2-Ethyl-1-hexanol	–	–	0.1	0.4	0.6	3.2	9.2	18.5	35.5	31.4
Phthalic anhydride	0.5	0.2	0.2	0.2	0.8	4.2	7.5	7.4	10.5	16.1
Methyl,2-ethylhexyl phthalate	0.3	0.1	0.1	1.7	4.2	7.1	8.1	7.2	1.9	0.2
Bis(2-ethylhexyl) phthalate	98.7	99.3	99.2	95.8	90.2	76.3	55.5	24.8	0.7	0.1

[a] Dilution ratio (by mol); carrier gas, N_2/sample = 20; residence time, 4.2 sec.

TABLE IV

Effect of Reaction Temperature on the Thermal Decomposition of Dioctyl Phthalate[a]

Component	Composition of decomposition products, wt %, at												
	250 C	280 C	300 C	320 C	340 C	350 C	360 C	380 C	400 C	420 C	450 C	480 C	500 C
1-Octene	0.4	0.3	0.2	0.5	1.7	2.1	2.0	5.2	8.4	20.3	43.9	60.4	57.2
Octanal	–	–	–	0.1	0.4	–	0.4	0.1	0.1	–	–	–	–
1-Octanol	0.4	0.5	0.4	0.4	0.5	0.5	0.6	1.0	3.4	10.1	22.1	24.5	22.6
Phthalic anhydride	0.1	0.1	0.1	–	–	0.2	–	0.5	3.0	6.3	4.3	4.5	8.8
Methyl,octyl phthalate	0.3	0.3	0.5	0.4	2.5	1.3	3.2	4.0	5.0	9.4	8.8	8.9	9.8
Dimethyl phthalate	–	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.4	0.6	0.2	0.1
Dioctyl phthalate	99.8	98.7	98.6	98.4	94.7	95.7	93.7	89.1	79.9	53.6	20.4	1.4	1.6

[a] Dilution ratio (by mol); carrier gas, N_2/sample = 20; residence time, 4.2 sec.

TABLE V

Effect of Reaction Temperature on the Thermal Decomposition of Didecyl Phthalate[a]

Component	Composition of decomposition products, wt %, at										
	200 C	250 C	300 C	350 C	380 C	400 C	420 C	450 C	480 C	500 C	525 C
1-Decene	3.0	3.5	3.7	5.4	20.8	24.2	33.3	53.4	59.0	60.1	72.8
Decanal	–	–	–	–	–	–	–	1.6	2.2	2.5	3.7
1-Decanol	–	–	–	–	–	7.9	8.7	10.9	17.0	18.1	14.5
Phthalic anhydride	–	–	–	–	4.4	5.9	9.4	12.4	16.7	12.3	10.8
Dimethyl phthalate	–	–	–	–	–	–	–	–	1.2	1.0	–
Methyl decyl phthalate	2.7	2.0	2.7	3.4	5.4	6.0	7.0	11.8	6.8	4.7	5.2
Didecyl phthalate	91.3	93.4	93.9	93.6	87.1	71.9	37.7	15.1	7.2	4.8	2.4

[a] Dilution ratio (by mol); carrier gas, N_2/sample = 20; residence time, 4.2 sec.

TABLE VI

Relationship between the Analytical Results of the Thermal Decomposition of Phthalic Esters and Its Boiling Points

Sample	Analytical results of the thermal composition of phthalic esters, wt %, at			Boiling point
	250 C	300 C	350 C	
Dibutyl phthalate	100	99.1	97.0	340 C/760 mmHg[b]
Dihexyl phthalate	99.7	99.9	94.4	220 C/5 mmHg[c]
Bis(2-ethylhexyl) phthalate	98.7	99.2	95.8[a]	231 C/5 mmHg[b]
Dioctyl phthalate	99.8	98.6	95.7	235 C/4 mmHg[b]
Didecyl phthalate	93.4	93.9	93.6	240∿245 C/3 mmHg[d]

[a] Reaction temperature at 360 C.

[b] C.I. Nass, Encyclopedia of PVC, Marcel Dekker Inc., New York, 1976, vol. 1, p. 522.

[c] I. Mellan, Industrial Plasticizers, Pergamon Press, New York, 1963, p. 159.

[d] Chem. Abstr. 50:251a (1956).

in much greater quantities. Tables I-V clearly show that every phthalic ester lost heat stability around its boiling point.

Table VI shows the relationship between the analytical results of the thermal decomposition of phthalic esters and its boiling points. We have no data on the accurate temperature for the thermal decomposition of phthalic esters, but the phthalic esters were unstable during the heat treatment, because thermal decomposition products were found below the boiling points for the phthalate esters.

Effect of Residence Time

Another important factor related to the heat stability in the thermal decomposition reaction is residence time. The result of the decomposition of dioctyl phthalate at various residence times is shown in Figure 4. In the apparatus shown in Figure 1, the residence time was varied from 5-20 sec in such a way that the feed rates of sample and the carrier gas were changed, keeping the reaction at a temperature of 430 C and the mixing ratio of the sample and the carrier gas constant (14). Figure 4 reveals that the decomposition of dioctyl phthalate increases from 55-85% in extending the residence time from 5-20 sec. Similarly, the production of 1-octene and octyl hydrogen phthalate increases linearly from 2.5-12% and from 1-13%, respectively. The diagram reveals, therefore, that the thermal decomposition of dioctyl phthalate is accelerated as the residence time is extended. Such a relationship between the amount of the decomposition product and the residence time was found to be applicable to the other phthalic esters.

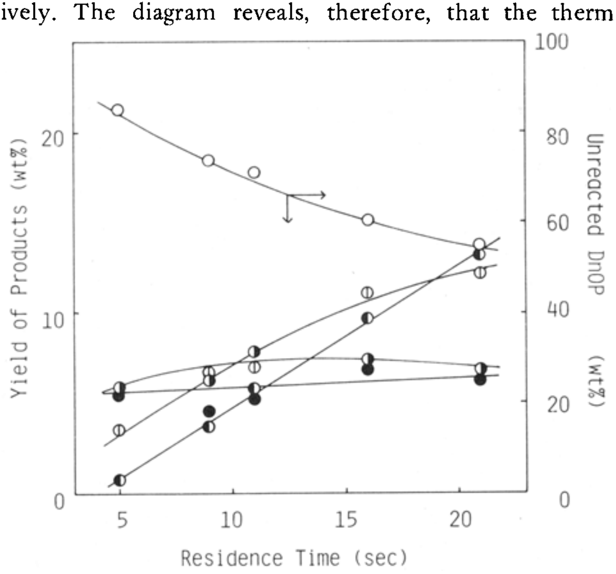

FIG. 4. Effect of residence time on the thermal decomposition products of dioctyl phthalate. Reaction temperature, 430 C; dilution ratio (by mol), carrier gas, N_2/sample = 20. Symbols: (⦶) 1-octene; (◑) 1-octanol; (◐) octyl hydrogen phthalate; (●) phthalic anhydride; (○) unreacted dioctyl phthalate.

Effect of PVC on Thermal Decomposition of Dioctyl Phthalate

The effect of PVC on the thermal decomposition of phthalic esters covers a wide area, e.g., human safety, the environmental problem in the working place where plasticized PVC is molded and air pollution by the potentially harmful substances emitted from the incineration of plasticized PVC waste (15,16). Understanding the thermal characteristics of phthalic esters is necessary, analyzing in detail the relationship between the phthalic esters and the heat stability of PVC, including the thermal decomposition products. The results shown in Figures 5 and 6 represent the relationship between PVC and phthalic esters. The detailed analytical method was described in another report (17).

Five wt percentages of commercially powdered PVC (containing Ba-Zn stabilizer) having an average molecular weight of 3,000 was added to dioctyl phthalate and the mixture was statically decomposed for 3 hours in a pyrex flask. Figure 5 shows the relationship between the conversion of the mixture and the reaction temperature. The result of dioctyl phthalate alone and that obtained in the flow reactor system are also shown. The figure reveals that PVC-promoted thermal decomposition reaction of dioctyl phthalate to such an extent that 5% was already decomposed at 150 C, which was about 100 C lower than the decomposition temperature of dioctyl phthalate alone. The thermal decomposition products were analyzed in more detail by GC to further investigate the effect of PVC (17). The relationship of the components of the decomposition product and the reaction temperature is shown in Figure 6.

The thermal decomposition products were 1-octene, 2-chlorooctane, phthalic anhydride and octyl hydrogen phthalate. Analytical results of 2-chlorooctane were as follows: IR (cm^{-1}): 670(C-Cl); GC-MS or high-MS (m/e): 112(M^+-HCl); ^{1}H-NMR ($\delta_{ppm}^{CDCl_3}$): 0.88(3H.m), 1.28(6H,m), 1.42(3H,s), 1.55(4H,m), 4.0(1H,q); ^{13}C-NMR ($\delta_{ppm}^{CDCl_3}$): 14.03(C_1), 22.61(C_2), 25.34(C_3), 26.65(C_4), 28.80(C_5), 31.72(C_6), 40.40(C_7), 58.87(C_8). The main thermal decomposition products were the same as those produced from dioctyl phthalate alone, proving that the thermal decomposition of dioctyl phthalate was also caused by *cis*-elimination in the presence of PVC. Many extremely small-quantity components (0.001% or less) ranging from compounds of low b.p. to those of high b.p. were observed on the GC chromatogram (17), illustrating that the thermal

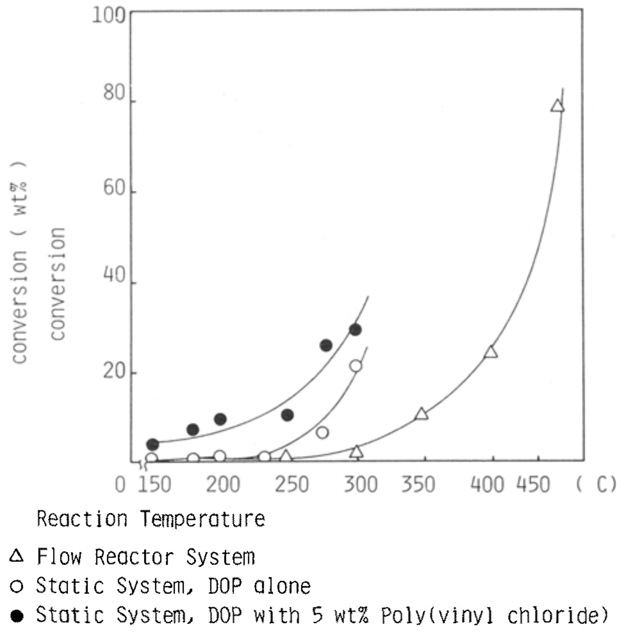

FIG. 5. Effect of reaction temperature on the conversion of dioctyl phthalate with or without PVC. Symbols: (△) flow reactor system condition, residence time 4.2 sec; dilution ratio (by mol), carrier gas, N_2/sample = 20; (○) static system, dioctyl phthalate alone; (●) static system, dioctyl phthalate with 5 wt % PVC. Condition: reaction time, 3 hrs under nitrogen gas; analytical methods (16).

decomposition followed complicated processes. 2-Chlorooctane, shown in Figure 6, is a compound that was identified for the first time in the thermal decomposition of phthalic esters; it has never been produced in the thermal decomposition of dioctyl phthalate alone. 2-Chlorooctane has the molecular structure of an addition compound from 1-octene produced from dioctyl phthalate and HCl produced from PVC. The presence of 2-chlorooctane in the decomposition product proved that the thermal decomposition products of dioctyl phthalate and of PVC interact with each other.

Considering that a large quantity of PVC and phthalic ester are heated for a long time (18) during preheating in the practical molding process of plasticized PVC, we estimate that the processes shown in Figures 5 and 6 will be more likely to happen and phthalic esters used for molding will be thermally decomposed easily.

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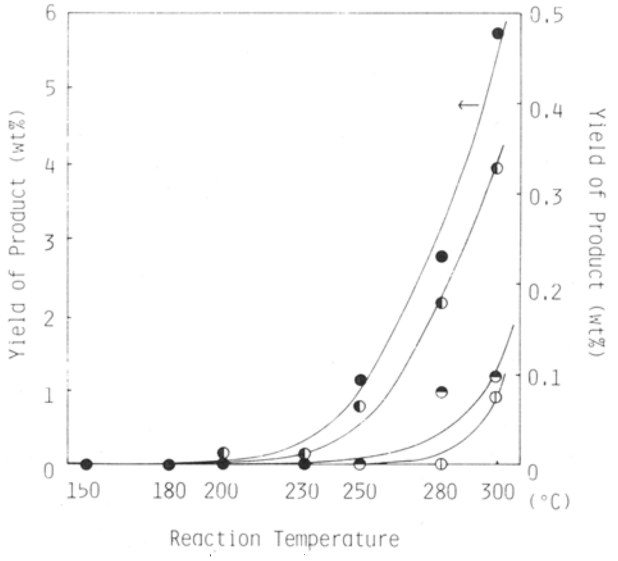

FIG. 6. Effect of reaction temperature on the thermal decomposition products of dioctyl phthalate with 5 wt % PVC. Condition: static system; reaction time, 3 hrs (under nitrogen gas). Symbols: (●) phthalic anhydride; (◐) methyloctyl phthalate(methyl ester for octylhydrogen phthalate); (⌽) 1-octene; (◓) 2-chlorooctane.

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