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Thermal Decomposition Products of Phthalates with Poly(vinyl chloride) and Their Mutagenicity

Katsuhiko Saido*, Hiroyuki Taguchi, and Satoru Yada
College of Pharmacy, NIHON University, 7-7-1 Narashinodai, Funabashi-shi, Chiba 274-8555, Japan

Yumiko Ishihara and Takeshi Kuroki
Polymer Decomposition Laboratory Co., Ltd., 2-12-7 Aoshima, Miyazaki-shi, Miyazaki 889-2162, Japan

In-Jae Ryu and Seon-Yong Chung
College of Engineering, Chonnam National University, 300 Yongbong-Dong, Buk-ku, Gwangju 500-757, Korea

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Abstract: The thermal decomposition of phthalate alone and with poly(vinyl chloride) (PVC) was carried out under a nitrogen atmosphere in a 4-necked separable flask. The thermal decomposition of phthalate in the presence of PVC began at 150°, about 100 °C lower than the decomposition of phthalate alone. The formation of octyl chloride indicated an interaction reaction between phthalate and PVC. From the analysis of the composition of commercially plasticized PVC sheet (film and board), the phthalates (dibutyl phthalate, dihexyl phthalate) and di(2-ethylhexyl) phthalate), 2-ethyl-1-hexanol, phthalic anhydride, and 2-ethylhexyl hydrogen phthalate were identified. The mutagenicities of these decomposition products were higher than those of phthalic diesters (phthalates).

Keywords: di(2-ethylhexyl) phthalate, dioctylphthalate, poly(vinyl chloride), thermal decomposition, mutagenicity.

Introduction

Poly(vinyl chloride) (PVC) is one of the main plastics produced in large quantities.[1] Phthalates are used as the main plasticizers and are generally added to PVC at up to 40 per hundreds resin (phr).[2] Phthalates from PVC can be found in the environment, and they have been identified as endocrine disruptors.[3] The plasticized PVC is heat-treated to around 200 °C during molding and processing.[4] Although it is known that plasticized PVC is partially decomposed thermally under such conditions, the details have not been studied.

The thermal decomposition of PVC,[5-8] and the metabolits[9] and toxicities[10] of the phthalates have been studied. However, the thermal stabilities of phthalates with PVC and the mutagenicities of the thermal decomposition products of phthalates with PVC have not been studied in detail. We studied the thermal decomposition of phthalates alone and with PVC under the same conditions, and the effects of PVC on the thermal decomposition of the phthalates were examined. The thermal decomposition products of the phthalates in commercial PVC products were also analyzed.

Experimental

Materials. Commercial di(2-ethyhexyl) phthalate (DEHP) and dioctyl phthalate (DOP) (Tokyo Kasei Co., Tokyo, Japan) were used after distillation. Additive-free PVC (average molecular weight: 3000 g/mol, Wako, Tokyo, Japan), and commercially available agricultural PVC film (0.2 mm thickness) and PVC board (4 mm thickness) were used. Extraction solvents, tetrahydrofuran (THF) and methanol were used after simple distillation. Diazomethane was prepared from *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide according to a published procedure[11] and the product was distilled with ether.

Analytical Procedures

Preparation of Analytical Samples. Figure 1(A) shows the preparation scheme of the thermal decomposition products of DEHP and DOP in the presence of PVC. Figure 1 (B) shows the analysis scheme derived from the phthalates in commercial plasticized PVC.

Decomposition Method and Apparatus. The thermal

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*e-mail : saidophd@pha.nihon-u.ac.jp

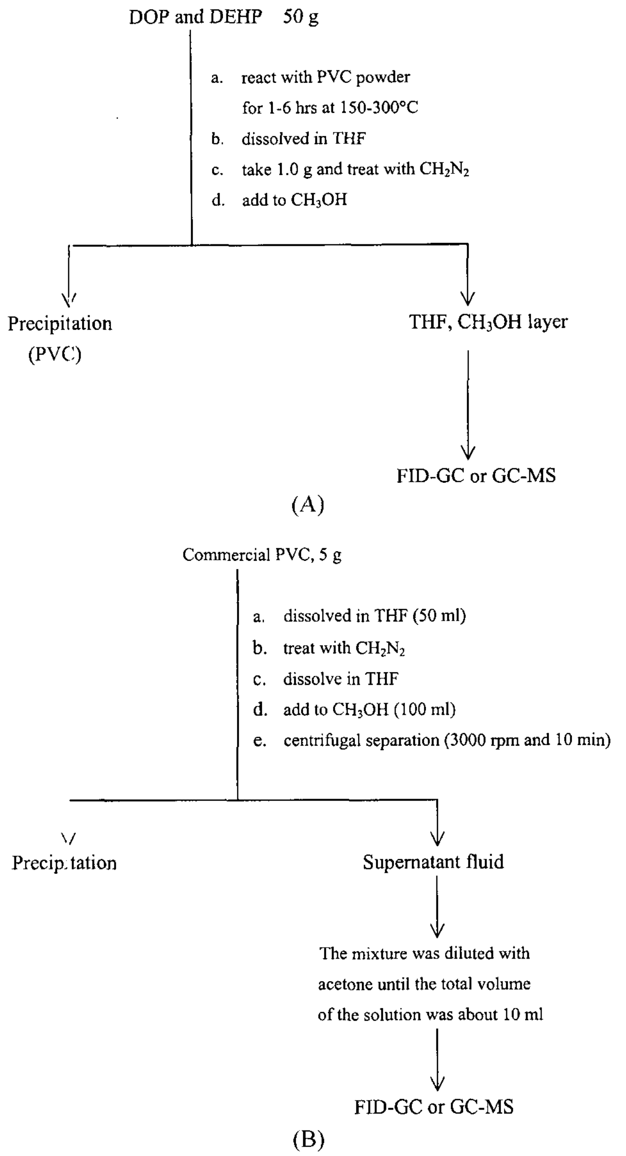

Figure 1. The schematic diagram of the analytical method for the components of the thermal decomposition products of DEHP and DOP in the coexistence of PVC.

decomposition reaction was carried out under a nitrogen atmosphere in a 4-necked separable Pyrex flask, equipped with a mechanical stirrer, a reflux condenser and a thermometer. A silicone oil bath was heated by an immersion heater to a temperature between 150-300 °C which was maintained within ± 3 °C by a temperature controller, Pulthermo (Toho Kagaku Co., Tokyo, Japan). For the identification of the decomposition products ^{1}H-NMR, ^{13}C-NMR, high-resolution MS, GC-MS and IR were used.

The gas chromatography (GC) procedure for the qualitative and quantitative analyses of the thermal decomposition products is as follows:

a. Model: Shimadzu GC-9APF (Kyoto, Japan) and C-R5A integrator equipped with a H_2-flame ionization detector.

b. Column: Silicone OV-17 2% on 60/80 mesh (Chromosorb WAW DMCS (GL Science, Tokyo, Japan)). 2 m Length, I.D. 3 mm.

c. Operation temperature: Injector 250 °C, detector 340 °C. Column 50 → 300 °C (heating rate: 20 °C/min).

d. Carrier gas: Nitrogen, 30 mL/min.

Rec Assay. Spores of *Bacillus subtilis* HA101 (rec+) and Rec-4 (rec-) were used for the assay.[12] The concentrations of each chemicals were diluted with acetone or DMSO in order to make the inhibition circle between I.D. 9 and 40 mm. The paper disks (I.D. 8 mm, Toyo Roshi Ltd., Japan) were placed on the broth culture with 107 spores/plate and 50 mL of the test solution were pipetted. The plates were incubated for 24 hrs at 37 °C. After the incubation, the diameters of inhibition zone were measured with calipers and the DNA damage index was calculated.

Results and Discussion

Thermal Decomposition of DOP Alone and with PVC. The products of DOP decomposition at 300 °C for 3 hrs in a static system were analyzed by the procedure shown in Figure 1(A). The analysis results are shown in Figure 2. Figure 2(A) shows the results from the DOP alone, while Figure 2(B) represents those from the DOP with 5 wt% PVC.

The conditions of the thermal decomposition and analysis for each samples were strictly the same. It is shown in Figures 2(A) and (B) that PVC accelerates the thermal decomposition of DOP with increasing the amounts of the thermal decomposition products. Every peak shown in Figures 2 (A) and (B) was identified by different instrumental analyses after being isolated by solvent extraction or by GC fractionation. One of the low boiling point components (peak 1) shown in Figure 2(B) was identified as 2-chlorooctane and the small peaks were derived from the thermal decomposition products of PVC.

The 2-chlorooctane was produced only in the presence of PVC and it corresponds to the compound from the HCl addition to 1-octene produced by the mechanism of the *cis* elimination[13] of DOP. This indicates that DOP reacts with the thermal decomposition products of PVC. It is clear that an interactive reaction exists between DOP and PVC.

The Effect of PVC on the Starting Temperature of the Thermal Decomposition of DEHP. In order to investigate the interaction between the phthalate and PVC, the thermal decomposition of DEHP with 5 wt% PVC was carried out 6 hrs under a nitrogen atmosphere. The results are shown in Figure 3.

The products were analyzed by the method shown in Figure 1(A). Figure 3 reveals that 1% of DEHP disappeared at 250 °C by the thermal decomposition of DEHP alone, while it started to decompose at 150 °C already in DEHP with 5 wt% PVC. Therefore, the starting temperature of decomposition

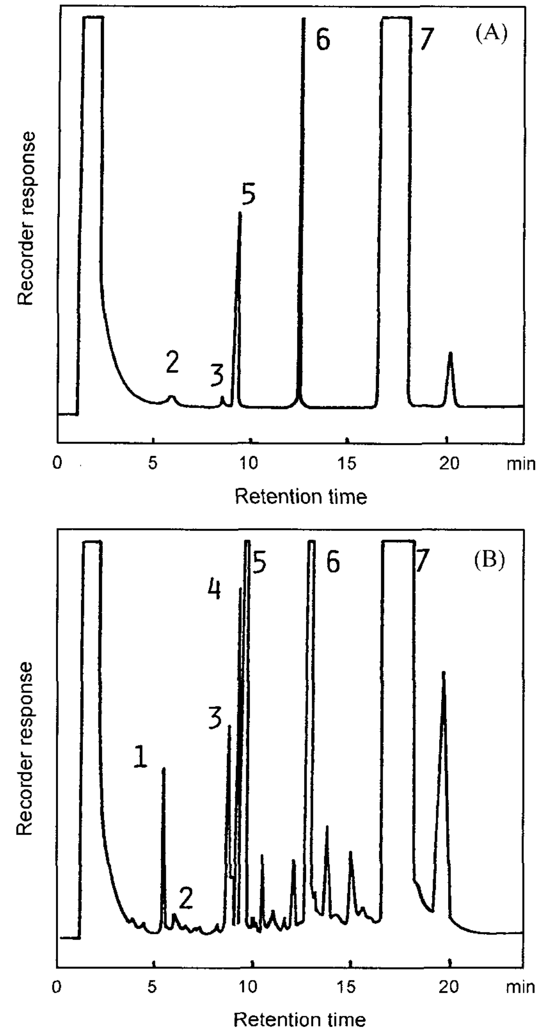

Figure 2. The gas chromatograms of the thermal decomposition products on dioctyl phthalate. (A) DOP alone and (B) DOP with 5% PVC added. Reaction temperature; 300 °C. Reaction time; 3 hrs. Column; Silicone OV-17 2% on Chromosorb WAW DMCS 60/80 mesh. Operating temperature; 50→295 °C (programmed speed 20 °C/min). Detector temperature; 340 °C. (1) 2-chlorooctane. (2) 1-octanol. (3) benzoic acid. (4) phthalic acid. (5) phthalic anhydride. (6) octyl hydrogen phthalate. (7) dioctyl phthalate.

was lowered by around 100 °C. Furthermore, 20% of the DEHP was decomposed at 300 °C. In the case of DEHP with 5 wt% PVC added, 32% of DEHP was decomposed. In the case of DEHP alone, on the other hand, 20% of DEHP was decomposed at the same temperature. It was revealed that PVC significantly affects the starting temperature of decomposition and the thermal decomposition reaction of DEHP. It was assumed that this was because the polarization of the ester bond was accelerated by HCl,[14] produced by the thermal decomposition of PVC.

The Effects of PVC on the Composition of the Thermal Decomposition Products of DEHP. The relationship between the reaction temperature and the various thermal decomposition products of DEHP in the presence of PVC is shown in Figure 4.

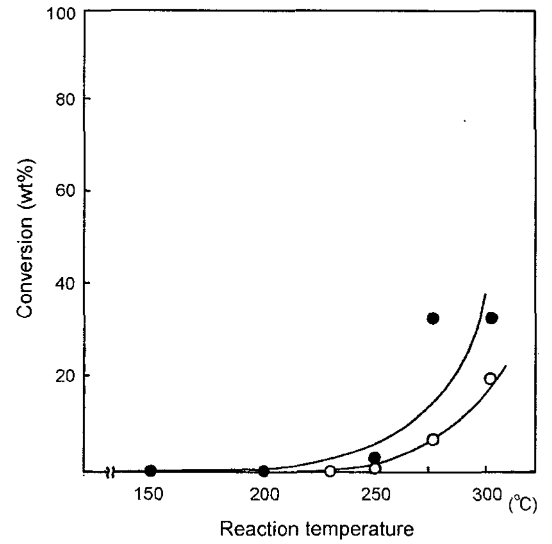

Figure 3. The effect of PVC on the starting temperature of the thermal decomposition of DEHP. Static system reaction time for 6 hrs. (○) DEHP alone and (●) DEHP with 5 % PVC added.

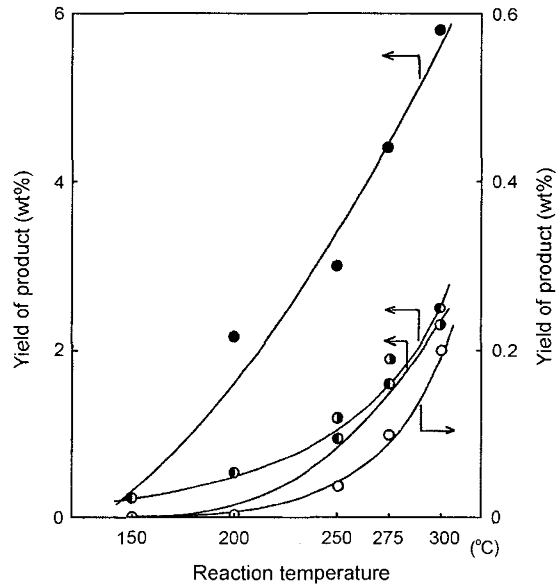

Figure 4. The effect of PVC on the composition of the thermal decomposition products of DEHP. Static system reaction time for 6 hrs. (○) octyl chloride. (◑) 2-ethyl-1-hexanol. (●) phthalic anhydride and (◐) 2-ethylhexyl hydrogen phthalate. The white circle was shown by right axis.

Figure 4 shows that the identified main components are phthalic anhydride and hydrogen phthalate. The principal mechanism of the thermal decomposition for DEHP is a *cis* elimination reaction[13] even in the presence of PVC. It was observed that the production of alkyl halide, such as chlorooctane, increased with increasing reaction temperature.

Plasticizers, such as DEHP or DOP are usually heated to approximately 200 °C in the mixing and molding processes of plasticized PVC. Since parts of DEHP are easily decomposed as shown in Figure 4, it is suggested that the low boiling point compounds, such as 2-ethyl-1-hexene, 2-ethyl-1-hexanol and octyl chloride, may pollute the working environment. High boiling point compounds, such as phthalic anhydride and 2-ethylhexyl hydrogen phthalate, are assumed to remain in the plasticized PVC.

The Mutagenicities of the Thermal Decomposition Products of Phthalate Alone and with PVC. It might be assumed that the acute toxicities of the phthalates were due to 30.6 g/kg of LD_{50} of DEHP measured by Shaffer *et al.*[6] Also, Singh *et al.*[15] found 50 g/kg of LD_{50} of DEHP in the same way. The hydrogen phthalates, which are intermediates of metabolism and of the thermal decomposition product of phthalates, indicate strong teratogenicity in the embryo. Nakamura *et al.*[16] showed that the hydrogen phthalate teratogenicities are 5 times stronger than phthalate. We measured the acute toxicities of the thermal decomposition products of the phthalates alone or with PVC using the Rec-assay. The DNA damage index of the thermal decomposition products of the phthalates alone and with PVC are shown in Table I.

In this method, there were no inhibition circles in the DOP or DEHP, but the thermal decomposition products of the phthalates alone or with PVC had DNA damage index between 0.38 and 2.6. These values did not indicate strong mutagenicity, but the hydrogen phthalates showed a stronger mutagenicity in 10^{-4} molar concentration. Table I shows that decomposition products such as chlorinated alkane, increased the toxicity compare with phthalates. The phthalates produced more toxic compounds during the thermal decomposition with PVC.

The Analysis of Commercial Plasticized PVC. The compounds derived from the phthalate in the plasticized PVC were extracted by the procedure shown in Figure 1(B). The analytical results by GC are shown in Figure 5.

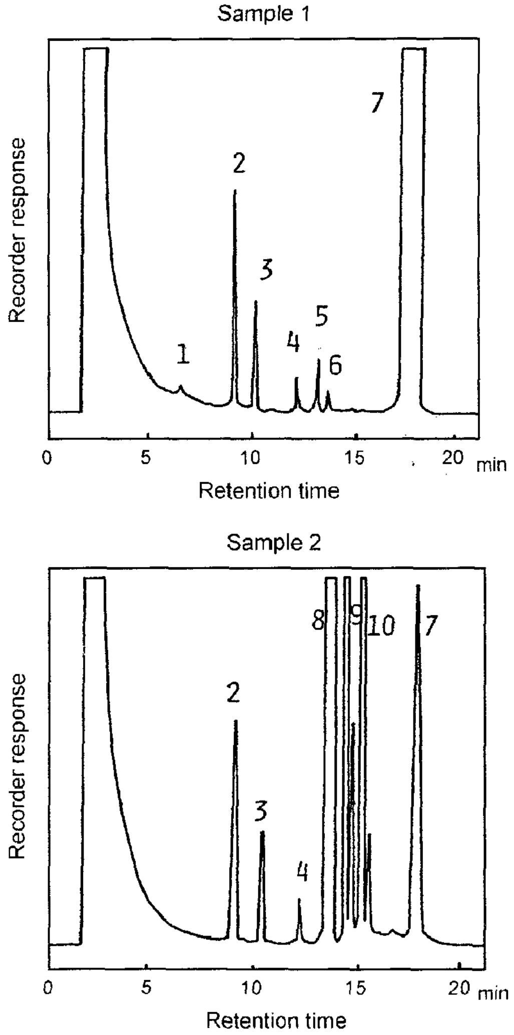

Figure 5. The GC analysis results of commercial plasticized PVC. Sample 1; agricultural plasticized PVC film 0.2 mm thickness, and Sample 2; plasticized 4 mm PVC board. (1) 2-ethyl-1-hexanol. (2) ethyl benzoate (internal standard). (3) phthalic anhydride. (4), (5) unknown. (6) 2-ethylhexyl hydrogen phthalate. (7) DEHP. (8) dibutyl phthalate. (9) dihexyl phthalate. (10) unknown.

Table I. The Effect of Mutagenicity on the DNA Damage Index

	The Least Concentration of Rec-Effect (mol/L)		DNA Damage Index
	Rec^+	Rec^-	
1-Chlorooctane	7.4× $10^{-2\,a}$	6.3× 10^{-2}	1.2
2-Chlorooctane	6.0× $10^{-1\,a}$	1.6	0.38
Phthalic anhydride	2.6× $10^{-2\,a}$	1.5× 10^{-2}	1.7
Phthalic acid	2.3× $10^{-2\,a}$	2.1× 10^{-2}	1.1
2-Ethyl-1-hexanol	3.6× $10^{-2\,b}$	2.7× 10^{-2}	1.3
Octyl hydrogen phthalate	7.2× $10^{-4\,b}$	4.6× 10^{-2}	1.6
2-Ethyl hexyl hydrogen phthalate	1.4× $10^{-3\,b}$	5.3× 10^{-2}	2.6

[a] Dissolve in acetone. [b] Dissolve in dimethylsulfoxide.

Sample 1 in Figure 5 shows an agricultural PVC film with 0.2 mm thickness, plasticized with DEHP. Sample 2 in Figure 5 shows a 4 mm PVC board plasticized with DEHP, dibutyl phthalate, dihexyl phthalate, etc. These figures show the thermal decomposition products derived from the phthalate in the samples 1 and 2. Peaks 1, 3 and 4 in the gas chromatogram were identified as 2-ethyl-1-hexanol, phthalic anhydride and 2-etylhexyl hydrogen phthalate, respectively. Peak 2 is an internal standard, ethyl benzoate, added to the sample to determine the recovered amount of it in the analysis process.

It was found that high boiling point compounds, such as phthalic anhydride, among the thermal decomposition products of the phthalic acid, produced by the thermal decomposition of the phthalate during the heat treatment of molding or processing of PVC, remained in the PVC product. The thermal decomposition of phthalates begins by way of a *cis* elimination[13] and finally produces 1-olefin, phthalic anhydride and the alcohol corresponding to the side chain. The determined amount of phthalic anhydride is equivalent to the decomposed phthalate.

The decomposed phthalate in each sample (50 g) of the commercial plasticized PVC were calculated from the calibration curve as follows: 2-ethyl-1-hexanol 0.01%, phthalic anhydride 0.07% and 2-ethylhexyl hydrogen phthalate 0.01% in Sample 1, and phthalic anhydride 0.07% in Sample 2. The amount of the final decomposition product (2-ethyl-1-hexene and 2-ethyl-1-hexanol) in Samples 1 and 2 was estimated to be 2.4×10^{-4} mol. It reveals that the low boiling point compounds produced by the decomposition of phthalates are emitted from the PVC product. Hayashi *et al.*[17] analyzed the same compounds in the atmosphere of plasticized PVC factories.

Conclusions

It was clear that the thermal decomposition of the phthalates was accelerated in the presence of PVC. And an interactive reaction was confirmed between the thermal decomposition products of the phthalates and PVC. Some alkyl halides were produced by an interactive reaction between the PVC and phthalates. The mutagenicities of the thermal decomposition products of the phthalates with PVC were higher than those of the phthalates alone.

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