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Degradation of Mixed Char of Poly(vinyl chloride) with Polyethylene Glycol to Give Hydrocarbons by the Reaction with Potassium Carbonate in Supercritical Water: Formation of Hydrocarbons Containing Lower Amounts of Benzene Accompanied by Formation of Water Soluble Potassium Salts of Carbon Oxides

Fuminori Akiyama

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577

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Degradation of char from poly(vinyl chloride) (PVC) or chars from mixtures of PVC and polyethylene glycol (PEG) with potassium carbonate in supercritical water was performed. Degradation of chars from a mixture of PVC and PEG prepared by heating at 250 °C in nitrogen atmosphere with potassium carbonate at 500 °C for 3 h in supercritical water gave a mixture of hydrocarbons in the yield of 11 wt%, in which the content of benzene was only 5%, accompanied by formation of oil in the yield of 16 wt%. The main reaction products in this degradation reaction were water soluble products. The facts that these water-soluble products did not any absorption in ^{1}H NMR and ^{13}C NMR spectra and that these water-soluble products show FT-IR absorptions at 1378 and 1622 cm^{-1} suggest that these water soluble products are potassium salts of carbon oxides.

Large amouns of poly(vinyl chloride) (PVC) have been produced industrially; the total extent in Japan is next to those of polyethylene (PE) and polypropylene (PP). Although the effective recycling techniques of PE or PP have been established,[1–14] no effective method for recycling of PVC has yet been established. Of widely used domestic plastics, PE, PP, polystyrene (PS), poly(ethylene terephthalate) (PET), and PVC, PVC is most problematic from the viewpoint of recycling. Thermal degradation of PVC gives hydrogen chloride and chlorinated hydrocarbons, which are corrosive and harmful, in addition to other hydrocarbons. Incineration of PVC results in formation of very toxic emissions such as polychlorinated dibenzodioxins (PCDD), dibenzofurans (PCDF), and polychlorinated biphenyls.

Most widely attempted approaches for recycling of PVC have employed thermal degradation. Thermal degradation of PVC has been known to give a mixture of volatile hydrocarbons, oil, char and hydrogen chloride.[15–20] In the thermal degradation of PVC, useful low molecular weight hydrocarbons were not formed in such large amounts. Of low molecular weight hydrocarbons formed in the degradation, benzene was often a main component.[15,18,20] In the previous paper it was reported that benzene was a main component in hydrocarbons formed by the reaction of PVC with potassium carbonate in the presence or absence of copper(II) oxide in supercritical water.[21] Tsuji et al. have reported that BTX was obtained in the yield of a little less than 10 wt% by the thermal decomposition of char from PVC in the presence of HZSM-5.[22,23] McNeil et al. have reported that thermal degradation of PVC at 500 °C gave liquid fraction in the yield of 7.0 wt%, in which the content of benzene was 80%. Therefore, the yield of benzene in their reactions was 5.6 wt%.[18] Miranda et al. have reported that thermal degradation of PVC at 520 °C gave light and heavy oils in the yield of 32.39wt%, in which the content of BTX were 27.32 wt%. Therefore, the yield of BTX in their reaction was 8.8 wt%.[20] In several reports concerning degradation of PVC including our report,[21] the yield of benzene is a little less than 10 wt% at most.

Although benzene is a useful chemical, in view of the combustibility of hydrocarbons, the mixtures of aliphatic hydrocarbons containing lower amounts of benzene are desirable. In the present research an effort to get a mixture of aliphatic hydrocarbons containing a lower amount of benzene was performed. Decomposition of char from a mixture of PVC and polyethylene glycol (PEG) by potassium carbonate in supercritical water gives a mixture of aliphatic hydrocarbons containing lower amounts of benzene. Another aim of the present report is to obtain an insight about water-soluble products formed by the degradation of PVC or chars from PVC by the reaction with potassium carbonate in supercritical water, and also water-soluble products obtained in the reaction of monochlorobiphenyl reported in the previous paper.[24]

Experimental

General Procedure. PVC (degree of polymerization n = 1100) and PEG (M_w = 20000) were purchased from Wako Pure Chemical Industry. LTD, and Nacalai Tesque Co, respectively. Analyses of aliphatic and aromatic hydrocarbons, and carbon dioxide were conducted using a Yanagimoto gas chromatograph G 2800 and a Shimadzu GC-14B, respectively. Analyses of organic products were conducted usingGLC columns of Unipak S and Porapaq Q and analyses of carbon dioxide was performed using GLC column of Unibeads C. Analyses and assignments of hydrocarbons were also based on the mass-spectroscopic data and gas chromatography obtained in previous studies.[25,26] FT-IR spectra of silver salts were measured using FT/IR-8300 of Japan Spectroscopic Co. LTD.

Preparation of Chars from PVC or Mixtures of PVC and PEG. Chars from PVC or chars from mixtures from PVC and PEG were prepared using a 52 mL stainless steel (sus 316) autoclave equipped with a gas inlet and a gas outlet, which is connected to traps cooled at −80 °C and a trap containing aqueous sodium hydroxide solution. PVC 16.5 g or 16.5 g of a mixture of PVC and PEG, weight ratio of which were 8/1, 6/1, or 4/1, were heated at 210, 230, 250, or 270 °C for 1 h in nitrogen stream, the rate of stream being 90 mL/min. Yield and elemental analyses of chars obtained are shown in Table 1.

Reaction of Chars from PVC or Mixtures of PVC and PEG with Potassium Carbonate in Supercritical Water. A 100 mL autoclave (Nitto Koatsu Co. LTD., Hastelloy X) was charged with 0.5 g of PVC or chars from PVC, 4 g of potassium carbonate, and 20 mL of water. The autoclave was cooled down to −20 to −30 °C, followed by being outgassed by vacuum and introduction of nitrogen gas several times. Then the autoclave was pressurized to 4 MPa or 2 MPa with nitrogen and the autoclave was heated to 500 or 550 °C, respectively, the pressure reaching to around 38 MPa during the reaction. After the autoclave was heated for 3 h at 500 or 550 °C it was cooled to room temperature. The autoclave was warmed to 120 °C and gas formed in the autoclave was transferred to a stainless steel gas storage tank, the temperature of which was kept at 120 °C so that benzene or toluene would not condense. Then the gas was analyzed.

Results and Discussion

When a mixture of char from PVC or chars from mixtures of PVC and PEG, potassium carbonate, and water was heated at 500 or 550 °C for 3 h, a mixture of hydrocarbons, acetone, and carbon dioxide, and residue was obtained. Reactions of several chars at 500–550 °C gave various mixtures of products as shown in Table 2. Inspection of Table 2 indicates that reactions of chars from a mixture of PVC and PEG give higher total yields of hydrocarbons and lower yield of benzene than reactions of chars from PVC. The reaction of char prepared from a mixture of PVC and PEG (weight ratio 6/1) at 250 °C gives about 11.0 wt% of hydrocarbons which contain only 5% of benzene (see Entry 7 of Table 2). Diminution of benzene formation in the reaction of mixed char of PVC and PEG compared to the reaction of char from PVC can be attributed to suppression of aromatization of PVC by PEG. PEG presumably exerts same effects on suppression of aromatization of PVC through two processes; char formation of PVC and degradation of the char. Firstly, PEG acts as a dehydrochlorination reagent for PVC. Inspection of Table 1 indicates that chars formed from a mixture of PVC and PEG at 250 °C (see Entries 4, 7, and 10) contains lower concentrations of chlorine atoms than char formed from PVC at 250 °C (see Entry 2). Miranda et al. reported that the chlorine content of the char formed from PVC at 250 °C was around 24 wt%,[20] this value being nearly the same as the present value of 26 wt% (Entry 2 in Table 1), considering differences of experimental conditions between vacuum pyrolysis (their case) and pyrolysis under nitrogen stream (our case). It has been reported that benzene forms during the dehydrochlorination process in thermal degradation of PVC.[19,27] Although polyene formed by the degradation of PVC is easily aromatized, double bonds formed by the assistance of PEG suffer suppression of aromatization by PEG molecules which combine with carbon atoms near the double bonds. Secondly, in addition to this effect, PEG presumably has some suppression effect of aromatization of PVC during degradation reaction of PVC.

Although one might suppose that chlorinated hydrocarbons such as chlorobenzene would be formed in these reactions, chlorobenzene and other chlorinated hydrocarbons were not formed because most chlorine atoms were captured as potassium chloride (vide infra). In addition to the fact that hydrocarbons formed in the present study are not contaminated by chlorinated hydrocarbons, the products contain only small amount of benzene. It has been considered that gasoline of high quality contains small amounts of aromatics.[3] Therefore, degradation of char from a mixture of PVC and PEG with potassium

Table 1. Yields and Elemental Analyses of the Chars Formed by Heating of the Mixture of PVC and PEG

Entry	PVC/PEG	Temperature	Yield	Elemental analyses /%		
	(weight ratio)	°C	wt%	C	H	Cl
1[a)]	PVC[b)]	210	88.6	50.36	5.14	28.98
2	PVC[b)]	250	56.5	66.84	6.28	26.35
3	8	210	65.7	51.82	5.89	31.93
4	8	250	40.4	71.09	7.05	13.16
5	6	210	78.3	47.44	5.68	32.17
6	6	230	61.8	57.08	6.36	24.40
7	6	250	49.2	67.84	6.84	13.76
8	6	270	41.1	76.94	7.23	10.04
9	4	210	73.1	48.99	6.09	30.09
10	4	250	46.0	64.17	6.74	18.39

a)Since this char is solid like tough glue, it was difficult to convert this char to a fine powder. Such a situation presumably brings about incomplete ignition of the char during elemental analyses, which brings about making ash and low value for chlorine content. b) PVC only.

Table 2. Yields of Hydrocarbons Formed by the Reaction of Chars of PVC or Chars from the Mixture of PVC and PEG with Potassium Carbonate in the Supercritical Water[a)]

Entry	PVC/PEG (weight ratio)	Temp (char formation /°C)	Temp (reaction) °C	Yield of products /wt%[b)]														
				Residue	C_1	C_2	C_3	C_4	C_5	C_6	C_{7+}	C_6H_6	C_7H_8	C_8H_{10}	Acetone	Total	HCO_3^-	CO_2
1	PVC[c)]	210	500	25	1.48	0.73	0.29	0.39	0.33	0.17	0.20	1.02	0.24	0.16	0.92	5.75	—[d)]	1.29
2	PVC[c)]	250	500	21	1.49	0.77	0.32	0.44	0.29	0.22	0.28	0.78	0.29	0.11	1.18	6.10	16.5[e)]	1.26
3	8	210	500	12	2.81	0.90	0.29	0.39	0.24	0.19	0.31	1.02	0.25	0.14	1.01	7.43	—[d)]	0.33
4	8	250	500	11	3.67	1.28	0.49	0.57	0.36	0.27	0.41	0.41	0.31	0.16	1.38	9.18	—[d)]	0.25
5	6	210	500	17	3.0	1.24	0.37	0.35	0.25	0.17	0.20	1.11	0.23	0.10	0.91	7.83	—[d)]	0.65
6	6	230	500	5	4.23	1.29	0.41	0.45	0.27	0.20	0.28	0.78	0.23	0.07	0.97	9.18	—[d)]	1.07
7[f)]	6	250	500	6	4.28	1.55	0.57	0.58	0.38	0.34	0.34	0.57	0.51	0.22	1.65	11.0	14.2[e)]	1.37
8	6	270	500	28	3.88	1.55	0.58	0.68	0.44	0.33	0.42	0.38	0.41	0.24	1.54	10.45	15.2[e)]	0.08
9	6	250	550	36	5.13	1.88	0.71	0.46	0.27	0.17	0.16	0.64	0.46	0.25	0.85	10.98	—[d)]	0.19
10	4	210	500	9	4.11	1.20	0.34	0.37	0.23	0.16	0.25	1.01	0.18	0.12	0.81	8.78	—[d)]	1.03
11	4	250	500	16	3.5	1.40	0.49	0.57	0.37	0.27	0.40	0.59	0.35	0.18	1.42	9.54	—[d)]	0.74

a) 0.5 g of char, 4 g of potassium carbonate, and 20 mL of water were used. b) Yields of hydrocarbon (C_n) is a summation of saturated and unsaturated hydrocarbons. c) PVC only. d) Not determined. e) carbon basis. f) Oil was extracted from the autoclave by washing using chloroform in the yield of 16 wt%.

carbonate in supercritical water can be considered to be good method for production of combustible fuel which does not contain corrosive or harmful materials. Oil was extracted from the autoclave used in Entry 7 of Table 2 by washing with chloroform in the yield of 16 wt%. In the other reactions in Table 2 similar adhesion of oil on the reaction vessel was observed. If this oil can be used as fuel, the yield of fuel is total 27 wt% (11 + 16), this value being a little lower than the results of Miranda et al.[20]

Yields of potassium hydrogencarbonate in Table 2 were determined by the method described in ref.24. Since these yields are nearly the same values as those reported in the reaction of monochlorobiphenyl with potassium carbonate in supercritical water,[24] yields of hydrogencarbonate were determined in only three reactions in Table 2. Therefore, it can be concluded that a part of chars from PVC or mixtures of PVC and PEG degradate to give carbon dioxide, which is converted to potassium hydrogencarbonate by the reaction with potassium carbonate and water.

It was reported in the previous paper[24] that 98.7% of chlorine atoms was captured as silver chloride by addition of aqueous silver nitrate solution to the resultant solution of the reaction of monochlorobiphenyl with potassium carbonate in supercritical water. If (Silver salts)$_{\mathrm{obsd}}$/(AgCl)$_{\mathrm{calcd}}$ is defined as a ratio of silver salt obtained to amount of silver chloride which is calculated from the chlorine content in the substrate, that ratio for the reaction of monochlorobiphenyl is 0.99.[24] Although a similar experiment was not conducted in the reaction of PVC with potassium carbonate in supercritical water,[21] such an experiment was now conducted and the amount of chloride ion was determined by the method described in the previous paper,[24] (Silver salts)$_{\mathrm{obsd}}$/(AgCl)$_{\mathrm{calcd}}$ being 1.0 for this case. These two values 0.99 or 1.0 for the reaction of or monochlorobiphenyl or PVC, respectively, seem to be a little too high in view of experimental error. For the reaction of chars from PVC or chars from mixtures of PVC and PEG, determination of chloride ion was conducted, taking care to decompose all contained carbonate or hydrogencarbonate by addition of dilute nitric acid, followed by warming to 70–80 °C before addition of aqueous silver nitrate solution;[24] the results are shown in Table 3. Inspection of Table 3 indicates that values for (Silver salts)$_{\mathrm{obsd}}$/(AgCl)$_{\mathrm{calcd}}$ for the reaction of chars from PVC are considerably higher than 1 and that the values for the mixed chars containing PEG in large amounts are small but exceed 1. The fact that (Silver salts)$_{\mathrm{obsd}}$/(AgCl)$_{\mathrm{cald}}$ exceeds 1 indicates that some anion other than Cl^-, which can react with Ag^+ and make precipitate of silver salts, is contained in the resultant aqueous solution of the reaction of the chars with potassium carbonate in supercritical water. In order to get insight into the structure of the anion, FT-IR spectra of these silver salts were measured taking care in making pellets to use the same amounts of the silver salts (6 mg) and potassium bromide (350 mg); results are shown in Fig. 1. This figure indicates that the larger the (Silver salts)$_{\mathrm{obsd}}$/(AgCl)$_{\mathrm{calcd}}$, the higher the absorptions at 1378 and 1622 cm^{-1} are and that small absorption at 1378 cm^{-1} can also be seen in the spectrum for the salt obtained in the reaction of PVC (not char) (see Fig. 1-C). The peak at around 1380 cm^{-1} or 1620 cm^{-1} is seen in the spectra of potassium carbonate or potassium hydrogencarbonate. Therefore, these spectra would be attributed to those of potassium salts of carbon oxides ($K_xC_yO_z$). When an aqueous solution formed by the reaction of PVC, chars from PVC, or mixed char of PVC and PEG with potassium carbonate in supercritical water was filtered to remove the residue and the filtrated aqueous solution was evaporated under vacuum, a white powder was obtained. The D_2O solution of this powder was revealed to have not any absorptions in ^{1}H NMR and ^{13}C NMR except by ^{1}H NMR absorption of H_2O. Since potassium carbonate or hydrogencarbonate does not give any absorption in ^{13}C NMR in ordinary measurement time, the fact that the water soluble powder does not have NMR absorptions also suggests that this powder formed by the above stated reactions of PVC or Chars from PVC is not an organic material but is a potassium salt of carbon oxide. Although one might suppose that alcohols or carboxylic acids were formed by the present reactions, in the GLC analyses of the products almost no alcohols were observed except for a trace amount of ethylene glycol in the reactions carried out using char from PVC and PEG. The

Table 3. Quantitative Analyses of Chloride Ion Formed by the Reaction of Chars from PVC with Potassium Carbonate in Supercritical Water at 500 °C

Entry	Char	Temp (°C) of char formation	(Silver salts)$_{obsd}$/(AgCl)$_{calcd}$
1	PVC	210	1.57
2	PVC	250	1.59
3	PVC–PEG (8/1)	210	1.17
4	PVC–PEG (8/1)	250	1.30
5	PVC–PEG (6/1)	210	1.20
6	PVC–PEG (6/1)	250	1.28
7	PVC–PEG (4/1)	210	1.12
8	PVC–PEG (4/1)	250	1.14

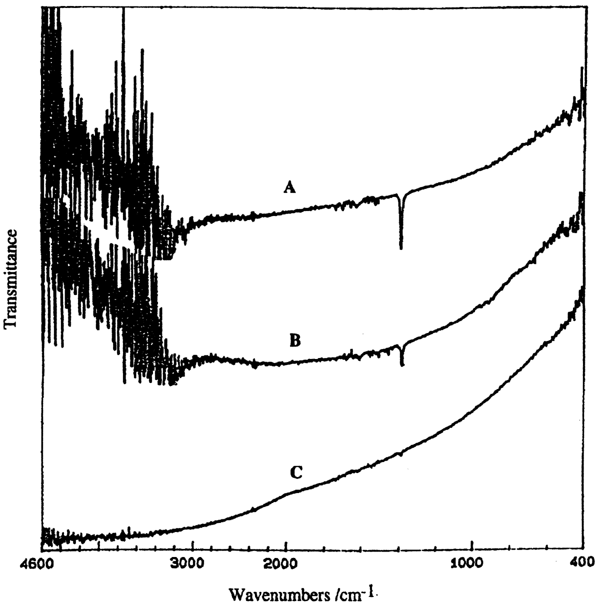

Fig. 1. FT-IR of silver salts obtained by the reaction of silver nitrate with the aqueous reaction solution of PVC or chars from PVC with potassium carbonate in supercritical water at 500 °C for 3 h. A: the reaction of char formed by heating of PVC at 250 °C (Entry 2 of Table 3); B: the reaction of char formed by heating of a mixture of PVC and PEG (4/1) at 210 °C (Entry 7 of Table 3); C: the reaction of PVC.

^{1}H NMR or ^{13}C NMR results of the above stated white powder obtained by evaporation of aqueous reaction solution did not show the presence of organic materials such as alcohols or carboxylic acids. Under these relatively severe reaction conditions water soluble organic materials, even if they are formed, presumably are decomposed to give stable hydrocarbons and acetone. Although the potassium salts of carbon oxides formed from the reaction of monochlorobiphenyl[24] or PVC are presumably easily decomposed with dilute acid, the potassium salt of carbon oxides formed from the reaction of chars from PVC are presumably not so easily decomposed by dilute acid. Therefore, the salts obtained by the reaction of chars from PVC give high values of (Silver salts)$_{obsd}$/(AgCl)$_{calcd}$ than the values for the silver salts obtained in the reactions of monochlorobiphenyl or PVC(not char). Quantification of the yields of potassium salt of carbon oxides is difficult because of their instability. FT-IR spectra of them changed when measurement was conducted a day after KBr pellet preparation. Prolonged drying under reduced pressure of the white powder, which was obtained by evaporation of the aqueous reaction solution, resulted in a decrease of weight. However, it is difficult to conclude whether this decrease of weight should be attributed to decrease of water content or to decomposition of the potassium salt of carbon oxides. Since the value of x, y, or z of potassium salts of carbon oxides ($K_xC_yO_z$) was not yet determined, determination of yields of them is impossible in the present stage of this research. Sako et al. have reported that organic carbons from the reactions of polychlorinated biphenyls with supercritical water-sodium hydroxide is only 50% of raw material. They have ascribed this discrepancy to formation of gaseous products without analyzing gaseous products.[28] Considering that their reaction temperature was lower than the temperature of our reaction in the present paper, we see that gaseous products would be formed in lesser yields in their reaction than in our study. The origin of the discrepancy between organic carbons formed and raw material in their reaction could also be ascribed to formation of water soluble inorganic salts.

Although yields of potassium salts of carbon oxides in the present study cannot be calculated since their structure cannot now be exactly determined, above all facts stated suggest that water-soluble potassium salts of carbon oxides are the main reaction products. If such a supposition is correct, the above stated degradations of PVC or chars from PVC are considered to be a sort of combustion. Since the reactions in the present study are carried out at lower temperature than ordinary combustion and the present reactions give not only CO_2 and carbon oxides salt but also hydrocarbons, the reactions can be called a mild incineration.

Conclusion

Degradation of chars from PVC or mixture of PVC and PEG with potassium carbonate in supercritical water at 500 or 550 °C gave a mixture of aliphatic and aromatic hydrocarbons, residue, carbon dioxide, potassium hydrogencarbonate, oil, and water soluble salts. Degradation of chars from a mixture of PVC and PEG gave larger amounts of hydrocarbons and lower amounts of benzene than the reaction of chars from PVC. Chlorine atom of PVC is quantitatively converted to potassium chloride by these reactions. The water soluble salts formed by the reaction of chars from PVC showed FT-IR absorption at 1378 and 1622 cm^{-1} and had no absorption in ^{1}H

NMR and ^{13}C NMR except for ^{1}H NMR absorption of H_2O, indicating that these water soluble salts are potassium salts of carbon oxides. The reactions are assumed to be a sort of mild incineration of PVC.

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