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DECOMPOSITION OF PCB's IN A HYDROGEN GLOW DISCHARGE PLASMA

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A study was made on the decomposition of PCB's in a radio-frequency glow discharge plasma of hydrogen. PCB's were completely decomposed in a plasma of hydrogen at 1 Torr. Major gaseous products were ethane, isobutane, and several higher hydrocarbons were recognized as minor products. Almost all of chlorine in PCB's was converted to hydrogen chloride.

Various methods have been reported for the decomposition of PCB's.[1-3] In our previous paper[1], the decomposition of PCB's in a low temperature glow discharge plasma of oxygen was described. It was found that PCB's were decomposed completely in an oxygen plasma into gaseous products with a very high efficiency. In this study, it was examined whether PCB's could be decomposed in a low temperature plasma of hydrogen. A detailed analysis of the reaction products was performed.

Samples of PCB's used were KC-200 and KC-500. Their empirical formulae were $C_{12}H_{7.99}Cl_{2.01}$ and $C_{12}H_{4.81}Cl_{5.19}$, respectively. The purity of the hydrogen gas used was 99.99999%. The general experimental procedures were very similar to those described in the previous paper[1].

Contrary to the decomposition of PCB's in an oxygen glow discharge plasma, a persistent brownish solid products were produced on the wall of the discharge tube when PCB's were subjected to a plasma of hydrogen. The solid products were found to be decomposed only very gradually but completely under the continuous stimulation by the hydrogen plasma for about 90 minutes.

The quantitative analyses of hydrogen chloride and chlorine were done by using the Mohr method and the redox titration method after the gaseous products were dissolved into the sodium hydroxide solution or the potassium iodide and sodium bicarbonate solution[1].

Fig.1 shows the dependence of the yield of the Cl^- ion on the hydrogen pressure. The total content of chlorine in PCB's corresponds to 100%. In all runs shown in Fig.1, no ClO^- ion was detected, i.e., the yield of Cl^- ion corresponds to that of hydrogen chloride.

As shown in Fig.1, the yields of Cl^- show maxima at about 1 Torr of the hydrogen pressure for KC-200 and KC-500. The decrease of the yields at low and high pressure regions could be explained as follows. The solid products produced on the wall of the discharge tube below 1 Torr was a firm deposit, and the lower the pressure, the harder the complete decomposition of solid products. At higher pressures, it was easier to decompose the solid products into gaseous products, however, the flow rate of the hydrogen gas became inevitably faster and some of the solid products were carried away from the plasma region down to the nitrogen cooled trap before they suffered a decomposition into gaseous products. The higher

Fig.1. Hydrogen pressure dependence on the yield of Cl^-

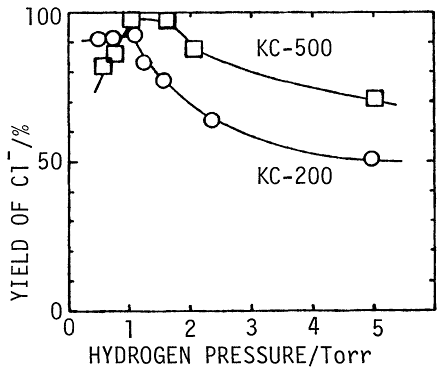
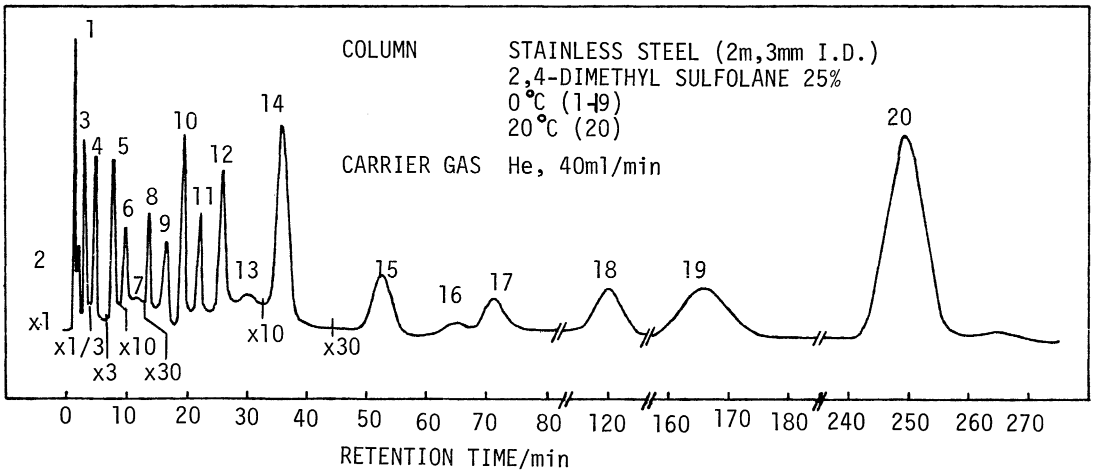


Fig.2. Gas chromatogram of gaseous products from the decomposition of KC-200



1) ethane (18.0)	8) 4-methyl-1-pentene (0.5)	15) 3-hexene (1.1)
2) propane (3.6)	9) 1-butyne (0.6)	16) cycloheptane (0.1)
3) isobutane (7.6)	10) cyclopentene (1.2)	17) 4-methyl-2-hexene (0.5)
4) butane (43.0)	11) methylcyclopentane (0.6)	18) not identified
5) 1-pentene (5.8)	12) 3-methyl-2-pentene (1.3)	19) 1,3-butadiyne (2.4)
6) 2-methyl-1-butene (1.1)	13) isopropenylcyclopropane (1.2)	20) benzene (4.6)
7) 2-methyl-2-butene (0.1)	14) 4,4-dimethyl-1-pentene (5.2)	

yield of Cl^- for KC-500 than for KC-200 may be due to the slower rate of vaporization of the KC-500 sample.

Fig.2 shows the gas chromatogram of the gaseous products from the decomposition of KC-200 in a plasma of 1 Torr hydrogen, obtained by using a Hitachi 063 gas chromatograph-mass spectrometer. The gas chromatogram of the gaseous products from KC-500 was very similar to the one shown in Fig.2. The most probable identification of peaks in Fig.2 was given below Fig.2. In the parenthesis is shown the relative amount (mol %) of each component. It is worthy to be noted that no chlorinated compounds were detected in the chromatogram, i.e., the conversion of chlorine in PCB's to hydrogen chloride was very efficient.

In summary, a GC-MS analysis showed that gaseous products from the decomposition of PCB's in a hydrogen glow discharge plasma at 1 Torr did not contain chlorine atoms. Almost all of the chlorine atoms in PCB's were converted to hydrogen chloride. This high yield of hydrogen chloride strongly suggests the efficient dissociative electron attachment reactions of chlorinated compounds in the plasma, i.e., the decomposition of negative ions into Cl^- and dechlorinated radicals. The Cl^- ion would be rapidly converted to HCl in a hydrogen plasma by the reaction $Cl^- + H = HCl + e$ whose rate constant is very large (0.96×10^{-9} cm^3/molecule·s).[4] Therefore, we would like to suggest that not only hydrogen atoms but also electrons play important roles for the decomposition of PCB's in a hydrogen glow discharge plasma.

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References and notes

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