

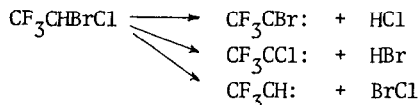
DECOMPOSITION OF SOME HYDROGEN-BEARING HALOGENATED ETHANES

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The decomposition of CF_3CHBrCl and $\text{CF}_2\text{BrCHClF}$ by thermal heating and by AC glow discharge were investigated with IR spectroscopy and GC mass-spectroscopy, etc. Thermal decompositions were made in glass vessels at pressures from 100 to 160 Torr of sample gases, whereas decompositions by discharge were made in a Kel-F reactor with nickel electrodes and at about 20 Torr.

Various halobutenes such as $\text{CF}_3\text{CH}=\text{CHCF}_3$, $\text{CF}_2\text{CH}=\text{CClCF}_3$, $\text{CF}_3\text{CBr}=\text{CHCF}_3$, $\text{CF}_2\text{CCl}=\text{CClCF}_3$, and $\text{CF}_2\text{CCl}=\text{CBrCF}_3$ were formed in the thermal decomposition of CF_3CHBrCl at 470°C . Eliminations of HCl and HBr were also found by IR spectroscopy. Then, the reactions may be explained by the following radical formations:



and their combination reactions.

In the thermal decompositions of $\text{CBrF}_2\text{CHClF}$ at 380°C , $\text{CF}_2=\text{CClF}$ was mainly formed by dehydrobromination in the early stage of the reaction. However, as the reaction proceeded, $\text{CF}_2=\text{CBrF}$ and $\text{CF}_2=\text{CHF}$ were additionally and increasingly formed. Their formation may be explained by substitution reactions between $\text{CF}_2=\text{CClF}$ and HBr. In the thermal decompositions at the temperatures above 420°C , those halo-ethylenes were not formed, but considerable amounts of hexafluorocyclobutene were formed.

After the thermal decompositions, the gases were cooled rapidly to room temperature, hydrolyzed in water, and the amounts of halide ions in the water were analyzed. In any thermal decomposition, the amount of chloride ions was larger than bromide ions. The amount of fluoride ions was always found to be very small.

In the case of glow-discharge, CF_3CHBrCl and $\text{CF}_2\text{BrCHClF}$ were both rapidly decomposed within 30 seconds. Similar reaction behavior was observed for both compounds as follows. Various halogenated methanes such as CBrF_3 , CCl_2F_2 , CBrClF_2 , and CF_4 were formed. When the discharges were continued further, the content of CF_4 increased gradually, and larger molecules and polymerized compounds were also increasingly formed.