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A PEROXIDE OF VINYL CHLORIDE

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Recently, a report was presented on conversion products of vinyl chloride and oxygen [1]. We would like to present some of our own results:

When subjected to UV irradiation between -15 and -20°C, vinyl chloride forms a peroxide $[\cdot OCH_2\text{-}CHCl\text{-}O\cdot]_n$. The compound, prepared in quantities of 60-240 mg, is a colorless, syrupy substance, the halogen atoms are readily split off by hydrolysis. On the basis of active oxygen, we obtained the substance in a purity of 80%. Cryoscopic molecular weight determinations in dioxane indicate n = 2. The compound can be hydrogenated with an excess of $LiAlH_4$ in tetrahydrofuran at 65°C into ethylene glycol (75% of theory) and HCl (85% of theory).

Thermal decomposition in an anhydrous CO_2-stream at 75°C, in part, takes place as follows:

$$[\cdot OCH_2\text{-}CHCl\text{-}O\cdot] \xrightarrow{\Delta} CH_2O + \left[\begin{matrix} Cl \\ | \\ C{=}O \\ | \\ H \end{matrix}\right] \longrightarrow CO + HCl$$

(39% d. Th.) (44% d. Th.) (79% d. Th.)

(39% of theory) (44% of theory) (79% of theory)

In the N_2-stream, 1-2% CO_2 are present.

At 50°C and 60°C, the thermal decomposition in dioxane still takes place at a measurable rate. In the hydrolysis with wet ether below 35°C, we found HCl (84% of theory), glycolaldehyde (20% of theory) and glycolic acid (26% of theory). The peroxide initiates the block polymerization of vinyl chloride above 35°C, but only a small quantity of polymer forms.

In a similar manner as vinyl chloride, 2-chlorpropylene, its methyl homolog, undergoes a reaction with O_2. However, we found

only 23% of the anticipated peroxide in the reaction product. In the reduction with $LiAlH_4$, propylene glycol was formed (18% of theory).

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1) G. A. Rasuwajew and K. S. Minsker: J. allgem. Chem. (Russ.) 28, 983 (1958).