

CONSTITUTION OF FLUOROFORM, CHLOROFORM, BROMOFORM AND IODOFORM.—PROTOTROPIC CHANGE.

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That chloroform gives with aqueous or alcoholic caustic potash CO gas was observed by Geuther (*Annalen*, 123, 121, 1862); Desgrez (*Compt. Rend.*, 125, 780–82, 1897) and Thiele and Dent (*Annalen*, 302, 273–74, 1898). The reaction with bromoform is slow, whereas iodoform is not acted upon at the ordinary temperature. G. Mossler (*Monatsch*, 29, 573–81, 1908) studied in detail the action of alcoholic KOH on CHCl_3 . The products of the reaction are CO, C_2H_4 and formate.

The classical reaction given in all text-books of organic chemistry is the following :—



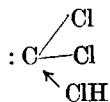
The formation of CO is not mentioned because it is looked upon by organic chemists as an irregular reaction.

Irregular reaction should, as a rule, be favoured by a rise of temperature; but on the contrary, the lower the temperature the more considerable is the evolution of CO. Richter in his text-book gave the following explanation :— By the action of alkali in the cold an intermediate reactive CCl_2 is formed which on hydrolysis gives rise to CO. With rise of temperature CO reacts with KOH to form formate as a secondary reaction product.

Chloroform, after the above reaction, appears as a hydrochloride of carbonous chloride.

Very recently Prof. G. Urbain (*Bull. Soc. Chim.*, 51, 853, 1932; *ibid.*, 53, 647, 1933) from the analogy of CHCl_3 with germanium and tin chloroforms supported the views of Richter and suggested CHCl_3 as a co-ordination compound of CCl_2 and HCl.

Expressed in modern electronic formula it appears—



as really a derivative of bivalent carbon.

Kuhn (*Ber.*, 60, 1297, 1927) has resolved the potassium salt of secondary nitroparaffins into its optical antipodes. Shriner and Young (*Journ. Amer. Chem. Soc.*, 52, 3332, 1930) have also confirmed it.

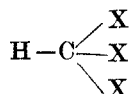
Sidgwick (*The Covalent Link in Chemistry*, p. 217; 1933) considers them as derivatives of tricovalent bivalent carbon (like : $\text{C} \equiv \text{O}$:) and suggests the

following structure for the anion : $\begin{array}{c} \text{R}^1 \\ \diagup \\ \text{C} - \text{R}_2 \\ \diagdown \\ \text{NO}_2^- \end{array}$ which will account for the molecular

dissymmetry—there being assumed a co-ordination link between carbon and nitrogen.

Prof. Urbain indicated the coincidence of the electric moment of HCl and CHCl_3 . Zappi (*Bull. Soc. Chim.*, 1453, 1935) considered that the reactivity of H of CHCl_3 could be demonstrated when the latter is dissolved in a liquid of high dielectric constant and of polar constitution such as pyridine. He thus tried to support the views of Urbain by determining the amounts of reactive hydrogen of CHCl_3 , CHBr_3 , and CHI_3 dissolved in pyridine solution with Zerewitnov's reagent. The amounts of reactive hydrogen were found in three cases to be respectively 100, 50, and 3 per cent. He concluded thereby that CHCl_3 is cent per cent of co-ordination structure, bromoform is a mixture of 50% normal and 50% co-ordination, whereas CHI_3 is a mixture of only 3% co-ordination and 97% normal structure.

A critical examination of various physico-chemical evidences does not go fully to support Urbain's views. Raman spectra definitely indicates the presence of CH linkage and the infra-red absorption spectra proves the absence of HCl in the molecule—thus supporting the classical formula—



The problem now poses how to explain the anomaly of observed chemical facts.

The intramolecular change brought about by the wandering of hydrogen atom from one position in the molecule to the other is named by Lowry—'Prototropy'. Since prototropy entails the migration of proton it is possible in many cases to isolate both isomeric forms in a pure state. Examples of the same may be cited in cases of Keto-enol forms of acetoacetic ester, normal and aci-forms of pseudo-acids.

The most effective catalysts, according to Lowry, in such prototropic changes are bases.

From the idea of prototropy we can explain the abnormal behaviour of fluoroform, chloroform, etc. Normally they should be represented by the

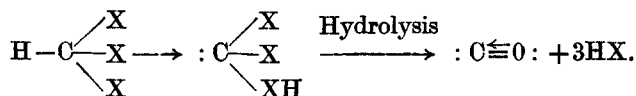
classical formula, $\begin{array}{c} \text{X} \\ \diagup \\ \text{H} - \text{C} \\ \diagdown \\ \text{X} \\ \text{X} \end{array}$. They are, however, susceptible to prototropic

change in presence of alkali in varying degrees in order of the electro-affinity of the halogens. The greater the electro-affinity the greater is the prototropic change.

Auger (*Bull. Soc. Chim.*, 5, 7, 1909) and Oechsner de Coninck (*ibid.*, 62-63) find that CHF_3 is decomposed by water and 95% of CO is obtained.

Thus fluoroform is more liable to prototropic change than CHCl_3 , bromoform still less and iodoform practically indifferent.

The change may be represented as follows :—



Thus the co-ordination structure proposed by Prof. Urbain is only an intermediate stage in the reaction of the molecule after the prototropic change—the carbon atom appearing to behave as a bivalent one.

The real cause of the difference in the behaviour of fluoroform and the allied halogen compounds lies in the comparative ease of the prototropic change and subsequent hydrolysis.

When the hydrogen of CHCl_3 is replaced by Me or Ph the abnormality at once disappears, that is to say, they do not liberate CO on treatment with alkali.

Mixture of CHCl_3 and alkali means the introduction of reactive $\text{>C} \begin{array}{l} \nearrow \text{Cl} \\ \searrow \text{Cl} \end{array}$ or reactive CO ($:\text{C}=\text{O}:$) group with incomplete octets. Mossler inferred the temporary formation of CCl_2 in explaining the formation of COCl_2 by passing CHCl_3 and air over alkali.

The *iso*-cyanide reaction of primary amines and the Riemer-Tiemann synthesis of phenolic aldehydes can be explained on this basis.

