ISOTOPIC INTERCHANGE REACTION BETWEEN CHLOROFORM AND WATER.

By J. HORIUTI and Y. SAKAMOTO.

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It is well known that chloroform decomposes when heated with alkaline solution in air. It was found now that in vacuum the isotopic interchange reaction between chloroform and heavy alkaline solution proceeds quicker than the decomposition.

Twenty c.c. of usually purified chloroform was sealed air-free in a reaction vessel of 80 c.c. capacity together with 0.5 c.c. of heavy alkaline, neutral or acidic solution. The reaction vessel was heated in a boiling water bath for a few days, opened and then the contents were separated from one another for analysis. The water of the solution or from the chloroform, which was burnt by a special furnace, was determined in density by means of a micro-pycnometer.[1] Part of the solution was tested for free chlorine ion by means of N/100 $AgNO_3$ solution in order to follow the decomposition of chloroform.

Solution	Time t (hours)	D-content in solution		D-content in chloroform after the reaction	k_i (hr^{-1}) $\times 10^4$	k_d (hr^{-1}) $\times 10^4$
		init. D_0	fin. D_t			
N/10 KOH	21	4.02	3.72	—	8	—
	72	,,	3.03	0.26	9	0.1
	60	,,	2.79	—	14	0.1
	48	,,	3.20	0.16	10	0.1
Pure water	85	3.14	3.18	—	0.4	—
N/100 H_2SO_4	15	2.91	2.86	—	3	—

(1) Okamoto and Shindo, *J. Chem. Soc. Japan*, **57** (1936), 669. The original method by Gilfillan and Polanyi, *Z. physik. Chem.*, A, **166**, 254 (1933), has since been essentially improved by these authors.

D-contents are given in terms of atomic percentage of deuterium. It is obvious from the table that the interchange reaction takes place with alkaline solution, which was confirmed by analysing both of the reactants. Interchange reaction with neutral or with acidic solution, if any, is far slower than that with alkaline solution.

Assuming the approximate chemical equivalence of H and D, the first order rate of interchange, $k_i \left(= \frac{2n_w}{n_{ch}} \frac{1}{t} \ln \frac{D_0}{D_t} \right)$, was calculated for chloroform from the decrease of D-content in the solution and this was compared with the rate of decomposition, $k_d \left(= \frac{n_{Cl'}}{3n_{ch}} \cdot \frac{1}{t} \right)$. n_w, n_{ch} and $n_{Cl'}$, are number of gram mols or gram ions of the water, the chloroform and free chlorine ions respectively. k_i or k_d is, therefore, the fraction of total quantity of chloroform which undergoes interchange (including the replacement of H atom of $CHCl_3$ by other H atoms from water or decomposition per unit time). We see from the figures in the table that a chloroform molecule is quickly interchanging its H atom with water before decomposition.

Detailed description of the experimental procedure and the discussion of the mechanism will be given later.

Chemical Department, Faculty of Science,
Hokkaido Imperial University.