ANOMALOUS SALT EFFECT ON THE RATE OF HYDROLYSIS OF CHLOROFORM.

An Additional Remark

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In the previous paper we reported that salt effect on the rate of hydrolysis of chloroform is anomalously large; namely that, in aqueous solution around pH 4, 0.01 N sodium sulfate decreases the rate about six-fold and 0.2 N sodium sulfate does sixteen-fold at least[1]. The pronounced salt effect has been accounted for by assuming an salt effect on elementary step (2) particularly when HA is H_2O in our reported mechanism[1)2)].

More detailed discussion is given here on the nature of the salt effect. The mechanism of hydrolysis of chloroform proposed by HORIUTI *et al.*[2] is quoted briefly.

$$CHCl_3 + B \longrightarrow CCl_3^- + H^+B \qquad (1)$$

$$CCl_3^- + HA \longrightarrow Cl_2C\overset{\times}{\underset{\times}{}}ClH + A^- \qquad (2)$$

$$B + Cl_2C\overset{\times}{\underset{\times}{}}ClH + HA \longrightarrow BH^+ + CCl_2 + ClH + A^- \qquad (3)$$

$$CCl_2 + H_2O \longrightarrow CO + 2HCl \qquad (4)$$

or

$$CCl_2 + 2H_2O \longrightarrow HCO_2H + 2HCl, \qquad (5)$$

where HA and B denote Brönsted acid and base respectively and $Cl_2C\overset{\times}{\underset{\times}{}}ClH$ an isomer of chloroform. In acidic region, step (2) controlls the hydrolysis, step (1) being in equilibrium. We shall now show that the pronounced salt effect leads necessarily to that on the activity of the critical complex of step (2). The observed rate of hydrolysis is, according to the mechanism, identical with the forward rate $\vec{v}$ of rate-determining step (2), which is expressed as $\vec{v} = k_2 a^{CCl_3^-} a^{H^+}$, where $a^{CCl_3^-}$ or a^{H^+} is the absolute activity of trichloromethyl anion CCl_3^- or hydrogen ion H^+. Since step (1) is in equilibrium, $a^{CCl_3^-}$ is fixed at the ratio a^{CHCl_3}/a^{H^+} of the absolute activity of chloroform a^{CHCl_3} to a^{H^+}. Therefore, $a^{CCl_3^-} a^{H^+}$ is kept constant independent of neutral salt concentration

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at constant pH, since a^{CHCl_3} is fixed at that of practically pure chloroform phase present under the experimental condition. The neutral salt effect comes hence into play only through the rate constant k_2 or the activity coefficient f^* of the critical complex according to the equation*) $k_2 = k_{2,0}/f^*$, where $k_{2,0}$ is the value of k_2 at infinite dilution of components of variable concentration, when $f^* = 1$. The f^* is thus varied by an amount which is hardly accounted for by the well-known neutral salt effect dealt with by Brönsted.

References

1) K. TANABE and Y. WATANABE, this Journal **7**, 79 (1959).
2) J. HORIUTI, K. TANABE and K. TANAKA, *ibid.* **3**, 147 (1955).
3) J. HORIUTI, *ibid.* **1**, 8 (1948).

*) For a step l in a homogeneous fluid, the forward rate $\vec{v}_l$ for unit volume is given as[3],

$$\vec{v}_l = \kappa \frac{kT}{h} \cdot \frac{Q^{\delta *}}{p^{\delta_l^I}},$$

where $Q^{\delta *}$ is the partition function of the critical complex[3] δ^* and the $p^{\delta_l^I}$ the BOLTZMANN factor of the chemical potential $\mu^{\delta_l^I}$ of the initial complex δ_l^I. Since $p^{\delta_l^I}$ is the reciprocal absolute activity according to a relation $RT \log a^{\delta_l^I} = \mu^{\delta_l^I}$, we have the following equations.

$$k_l = \kappa \frac{kT}{h} Q^{\delta *} \qquad \text{or} \qquad k_l = k_{l,0}/f^*,$$

where

$$k_{l,0} = \kappa \frac{kT}{h} Q_0^{\delta *} \quad \text{and} \quad f^* = Q_0^{\delta *}/Q^{\delta *}$$

is the statistical mechanical expression for the activity coefficient of the critical complex δ^* of the step and $Q_0^{\delta *}$ the particular value of $Q^{\delta *}$ at infinite dilution of components of variable concentration.