KINETICS OF ACETONE IODINATION IN ACID MEDIUM

1. PURPOSE OF THE WORK

Determination of the rate constant of the iodination reaction of acetone in an acid medium.

2. THEORETICAL NOTIONS

The process of iodination of acetone in an acid medium, characterized by the global equation

$$CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + HI \tag{1}$$

it involves a slow stage of enol formation and a rapid stage of its iodination. The enol formation stage involves two stages. The first step is protonation of acetone. A hydrogen atom from a methyl group becomes labile under these conditions and restores the hydroxonium ion with a molecule of water to give the enol.

This reaction (with speed constant k_1) proceeds slowly. Thus, the first step of the reaction is the tautomeric conversion of acetone to enol. The next stage is the reaction of enol with I_2 (rate constant k_2), a reaction that occurs very quickly ($k_2 > k_1$):

$$CH_3-\overset{\overset{\displaystyle OH}{|}}{C}=CH_2 + I_2 + H_2O \longrightarrow CH_3COCH_2I + H_3O^+ + I^- \tag{2}$$

The overall speed of the process will be given by the speed of the slow process, ie the process of enol formation (first stage). It is observed that in the iodination step of the enol, H_3O^+ is formed which contributes to the realization of the enol formation step, increasing the speed of this process. These self-accelerating processes are called *autocatalytic reactions*. The speed of the overall process, being determined by the first stage, depends on the concentration of acetone and acid and not on the concentration of iodine. If a is the initial concentration of acetone, b - the initial concentration of the acid, and x - the decrease in the concentration of acetone, at a time t of the reaction, the concentrations will be (a - x) mol / L acetone and (b + x) mol / L acid.

The reaction speed will be:

$$\frac{dx}{dt} = k(a-x)(b+x) \tag{3}$$

Integrating the above differential kinetic equation, by decomposition into simple fractions, the relation is obtained:

$$k = \frac{1}{t(a+b)} \ln \frac{a(b+x)}{b(a-x)} \qquad [conc^{-1}\ timp^{-1}] \tag{4}$$

If the initial concentrations *a* and *b* are taken equal, we obtain:

$$k = \frac{1}{2at} \ln \frac{a+x}{a-x} \qquad [\text{conc}^{-1}\ \text{timp}^{-1}] \qquad (5)$$

Since x << a, it follows that $\ln \frac{a+x}{a-x} \approx \frac{2a}{a} \left(1 + \frac{x^2}{3a^2} + ...\right)$ (6)

so

$$k = \frac{x}{a^2 t} \left(1 + \frac{x^2}{3a^2}\right) \qquad (7)$$

The decrease in acetone *x* concentration is determined by titrating unreacted iodine with thiosulphate in the presence of starch.

3. EXPERIMENTAL PART

3.1. APPARATUS AND SUBSTANCES

- automatic titrimeter, 250 mL rated flask, Erlenmeyer flask, 25 mL pipette, 25 mL bubble pipette, magnetic bar, stopwatch, I_2 0.1 N in KI solution, 1 N HCl solution, distilled water, acetone, sodium bicarbonate 0.1 N solution, starch, 0.01 N sodium thiosulfate solution.

3.2. PROCEDURE

The reaction takes place at room temperature. Into a 250 mL volumetric flask, place 25 mL of 0.1 N I_2 solution in KI and 25 mL of 1 N HCl solution, measured with a pipette. Then add approx. 150 mL of distilled water (practically until the level of liquid in the flask reaches the point where the neck of the flask begins). To an Erlenmeyer flask fitted with a magnetic stirrer is added 25 mL of 0.1 N $NaHCO_3$ solution. 1.8 mL of pure acetone is added to the volumetric flask and brought to the mark very quickly with distiled water. Shake the balloon. Start the stopwatch. Using a 25 mL bubble pipette, take the sample which is placed in the Erlenmayer beaker containing 25 mL of 0.1 N $NaHCO_3$. The bicarbonate solution is intended to stop the reaction.

The time of sampling immediately after the reaction has begun is the initial time. At first the reaction is slow, increasing its speed as the acidity of the environment increases. Therefore, the few moments that are lost at the beginning of the reaction do not introduce sensitive errors. The sample thus taken is titrated with 0.01 N sodium thiosulphate in the presence of starch. Titrate to yellow. Add starch and continue the titration until the color disappears. Wash the beaker carefully to recover the magnetic stirrer and prepare with 25 mL 0.1 N $NaHCO_3$ solution.

The following samples (25 mL) are taken every 10 minutes from the start of the reaction (see table of experimental results).

4. PROCESSING OF EXPERIMENTAL DATA

4.1. The experimental data are entered in a table of the form:

t, min	**v_t, mL**	**x, mol/L**	**k, $min^{-1}\cdot mol^{-1}\cdot L$**
0			
10			
20			
30			
40			
50			
60			

4.2. If v_0 and v_t are volumes of initial thiosulphate and at time t (in mL), the concentration change at this time will be

$$x = \frac{v_0 - v_t}{v_p} \cdot c \tag{8}$$

where:

c - concentration of thiosulphate solution (mol / L)

v_p - sample volume (mL).

4.3. The initial concentrations of HCl and acetone will be calculated as follows:

- initial concentration for HCl (**notation b**):

$$c'_{HCl} \cdot V'_{HCl} = b \cdot V_t \tag{9}$$

where:

c'_{HCl} - HCl concentration before mixing

V_t - total volume of the reaction mixture

V'_{HCl} - the volume of HCl before mixing

- initial concentration of acetone (**notation a**):

$$a = \frac{n_{acetone}}{V_t} = \frac{\frac{m_{acetone}}{M_{acetone}}}{V_t} = \frac{\rho_{acetone} \cdot V_{acetone}}{M_{acetone} \cdot V_t} \text{, mol/L} \tag{10}$$

4.4. Calculate the rate constant for each time, then make the arithmetic mean. Use relation (4) in case a ≠ b, or relation (5) in case a = b;

4.5. Considering the experimental value of the rate constant and the initial acid concentration 0.001 M, draw the graph $x = f(t)$ from $x = 0$ to $x = 0.095$.

Data from the literature

$M_{HCl} = 36.46\, g/mol$ $M_{(CH_3)_2CO} = 58.08\, g/mol$ $\rho_{(CH_3)_2CO} = 791\, g/L$

5. QUESTIONS

5.1. Integrate relation (3) by the method of decomposition into simple fractions, in order to obtain the velocity constant *k*.

5.2. What form does the dependence of the reaction rate on time have in the case of autocatalytic reactions?