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BRIEF COMMUNICATIONS

Utilization of N,N-Dichloro-p-chlorobenzenesulfonamide

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Abstract—The kinetic parameters of the reaction of *N*,*N*-dichloro-*p*-chlorobenzenesulfonamide with hydrochloric acid were determined, and the main parameters of the commercial process were estimated.

In the context of elimination of chemical weapons, a problem arises of utilization of agents used for rendering war gases harmless. One of such agents is N,Ndichloro-p-chlorobenzenesulfonamide (**I**, Russian commercial name DTKh-2). Owing to the high reactivity of the N–Cl bond, a promising way of its utilization is replacement of active chlorine atoms by hydrogen atoms with the formation of p-chlorobenzenesulfonamide (**II**), which can be used for synthesis of sulfamide drugs, dyes, and effective means for plant protection [1-3]. For this process, a reagent should be chosen that would be cheap and readily available and would give the minimum amount of minor or difficult-to-trap products. One of such agents is hydrochloric acid.

The goals of this study were to determine the kinetic characteristics of the reaction of \mathbf{I} with HCl and estimate the main parameters of the commercial process.

EXPERIMENTAL

The reaction was performed in a glass vessel equipped with a jacket and a thermometer. The vessel was charged with 10 g of **I**, after which 50 ml of 2 N HCl (equivalent excess 0.34 mmol) was added, and the solution was heated to a required temperature (77 or 92° C) under stirring with a magnetic stirrer.

The experimental conditions should be chosen so as to ensure the most active reaction (i.e., to eliminate possible diffusion hindrance); the optimal temperature and concentration should be determined. Preliminary experiments showed that at a stirrer rotation rate of no less than 700 rpm the conversion is independent of the stirring rate. The suitable reaction temperature is restricted by the thermal stability of the melt of **I** under water (up to 95°C [4]); 2 N HCl is convenient as it is sufficiently concentrated, but does not fume yet. Also, it is known that in more concentrated HCl the solubility of chlorine increases, which complicates its separation.

At appropriate intervals, we sampled the reaction mixture to determine the HCl concentration by alkali titration. Samples of the solid phase were analyzed for available chlorine by iodometric titration [5] after drying to constant weight and dissolution in a 1 : 1 mixture of 1,2-dichloroethane and glacial acetic acid. When calculating the conversion, we took into account the variation of the molecular weight of the solid phase in the course of the reaction.

Amide II was identified by the melting point $(143 \pm 1^{\circ}C)$; according to [4], 143–144°C) and IR spectrum. The IR spectra of I and II in mineral oil were measured on a Specord-80 spectrophotometer. The spectrum of II shows two bands (3332 and 3240 cm⁻¹) belonging to antisymmetric and symmetric stretching vibrations of the NH₂ group. Such bands are absent in the spectrum of I.

Figure 1 shows as a function of time τ the conversion η with respect to available chlorine (1, 3) and HCl (2, 4), at 92 and 77°C; the conversion with respect to HCl was calculated by the formula

$$\eta = 1 - (C - \overline{C})/(C_0 - \overline{C}), \qquad (1)$$

where C, \overline{C} , and C_0 are the current, excess, and initial concentrations of HCl, respectively.

It is seen from the figure that the conversion is complete only with respect to dichloramide I (with respect to HCl, $\eta < 1$). This means that reversible reaction [4] is shifted to the right (owing to removal



Fig. 1. (a) Conversion η with respect to (1, 3) available chlorine and (2, 4) HCl vs. time τ ; (b) linearization of curves *1* and *3* in the coordinates $\ln(1 - \eta) - \tau$. Temperature, °C: (1, 2) 92 and (3, 4) 77.

of chlorine) and that HCl is not only consumed, but also formed (most probably, by reaction of chlorine with water):

p-ClC₆H₄SO₂NCl₂ + 2HCl $\rightleftharpoons p$ -ClC₆H₄SO₂NH₂ + 2Cl₂. (2)

Therefore, the kinetic parameters were calculated only from dependences 1 and 3 linearized in the coordinates $\ln(1 - \eta) - \tau$ (Fig. 1b).¹ From the slope of the straight lines we determined the rate constants of removal of available chlorine k, and from their temperature dependence we estimated the activation energy of the process to be 89.1 kJ mol⁻¹.

Then, in the formula for calculating the conversion of available chlorine

$$\eta = 1 - \exp(-k\tau) \tag{3}$$

the rate constant k (h⁻¹) is

$$k = 3.6 \times 10^{12} \exp(-89\,100/RT). \tag{4}$$

where $R = 8.314 \text{ J} \text{ mol}^{-1} \text{ K}^{-1}$.

The experimentally estimated activation energy confirms the assumed kinetic control of the process.

Formulas (3) and (4) allow approximate estimation of the most important parameter of the commercial process, specific output V of a reactor of unit volume. If the reaction is performed at 92°C to 98% conversion, then, according to formulas (3) and (4), the residence time will be 5 h; hence, $V = 40 \text{ kg m}^{-3} \text{ h}^{-1}$, i.e., the specific output is moderate.

A significant factor in this process is stirring. Calculation of the power of the electric stirrer according to [6] gave a value of 0.65 kW m⁻³. The heat consumption for heating of the reaction volume (1 m^3) is 0.1 Gcal. It is seen that the power consumption is low. Note also that the released gaseous chlorine can be readily absorbed in a standard alkaline absorber [7] to form a valuable product, hypochlorite.

Thus, the proposed procedure for utilization of I is attractive owing to the low power consumption and low environmental impact.

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¹ Linearization of dependences 1 and 3 in the coordinates of a first-order reaction equation is probably due to the mutual compensation of two opposite processes: acceleration owing to additional formation of HCl and deceleration owing to the reaction reversibility. Therefore, the constants determined in this work should be regarded as apparent.