Kinetics of Dehydrochlorination of 2,3,4-Trichloro-1-butene and 2,3,3-Trichloro-1-butene by Methanolic Solution of Sodium Hydroxide

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Rate constants of dehydrochlorination of 2,3,4-trichloro-1-butene and 2,3,3-
-trichloro-1-butene by methanolic solution of sodium hydroxide at temperatures $0-60°C$ were measured and the appropriate activation energies were calculated. The results showed that the reaction rate of dehydrochlorination of 2,3,4-trichloro-1-butene was at 40°C 436 times greater than that of 2,3,3-
-trichloro-1-butene. The activation energy for the first reaction was 17 ± 0.5 kcal mol^{-1}, the frequency factor $A_{2,3,4-TCB} = 1.014 \times 10^{11} \pm 1.33 \times 10^9$ l mol^{-1} s^{-1} and that for the second reaction was 20 ± 1.2 kcal mol^{-1}, the frequency factor was $A_{2,3,3-TCB} = 4.094 \times 10^{10} \pm 1.75 \times 10^9$ l mol^{-1} s^{-1}.

2,3,4-TCB is used for the production of 2,3-dichloro-1,3-butadiene which is suitable for copolymerization with chloroprene [1]. It is prepared by chlorination of 1,3-dichloro-
-2-butene which is a by-product in chloroprene production [2]. A great amount of 1,2,3,3-tetrachlorobutane, formed in this reaction as addition product, gave also 2,3-
-dichloro-1,3-butadiene after elimination of two molecules of hydrochloride [4]. Dehydrochlorination to the first step only gives mainly 2,3,3-TCB [11], from which it is more difficult to eliminate hydrochloride than from 2,3,4-TCB regarding the position of chlorine atom in the molecule.

The aim of the present work was to compare the reaction rates of dehydrochlorination of the mentioned trichlorobutenes by methanolic solution of sodium hydroxide under conditions determined as optimal for dehydrochlorination of 2,3,4-TCB [3].

Experimental

Chemicals

2,3,4-TCB prepared according to [2], rectified, had n_D^{20} 1.4941, ϱ_4^{20} 1.3426 (n_D^{20} 1.4944, ϱ_4^{20} 1.3430 [5]). Its purity established by gas chromatography was 97.6% [7].

2,3,3-TCB prepared according to [3], rectified, had n_D^{20} 1.4809, ϱ_4^{20} 1.3055 (n_D^{20} 1.4815, ϱ_4^{20} 1.3067 [6]). Its purity established by gas chromatography was 93%.

Methanol and sodium hydroxide were of anal. grade.

Abbreviations:

2,3,4-TCB = 2,3,4-trichloro-1-butene.
2,3,3-TCB = 2,3,3-trichloro-1-butene.

Working procedure

Kinetic measurements were carried out in a vertical, cylindrical glass vessel (22 × × 122 mm) fitted with a stirrer and a thermometer. The vessel was placed in a Höppler thermostat. To a methanolic solution of trichlorobutene of a chosen temperature, the corresponding amount of methanolic solution of sodium hydroxide was added from a tuberkulin syringe under stirring. The starting concentration of 2,3,4-TCB was $4.925 \times \times 10^{-2}$ mol l^{-1} and that of 2,3,3-TCB 1.6 mol l^{-1}. The reacting components were in equimolar ratio. The reaction was stopped by adding an excess of nitric acid and the whole volume of the reaction vessel was analyzed.

The conversion of trichlorobutene was determined by titration of the formed chlorides after Volhard.

Results

Rate constants were calculated from the relation characterizing reactions of the second order. Values of the rate constants are listed in Table 1.

The relative rate of reactions $v_{rel} = 436.2$ was calculated from comparison of the rate constants ($k_{2,3,4\text{-TCB}}$ and $k_{2,3,3\text{-TCB}}$) at 40°C.

The activation energies were calculated from Arrhenius equation. For dehydrochlorination of 2,3,4-TCB by methanolic solution of sodium hydroxide, the activation energy was 17 ± 0.5 kcal mol^{-1} and that for dehydrochlorination of 2,3,3-TCB was 20 ± 1.2 kcal mol^{-1} and the appropriate frequency factors were $A_{2,3,4\text{-TCB}} = 1.014 \times 10^{11} \pm 1.33 \times \times 10^9$ l mol^{-1} s^{-1} and $A_{2,3,3\text{-TCB}} = 4.094 \times 10^{10} \pm 1.75 \times 10^9$ l mol^{-1} s^{-1}.

Table 1

Rate constants of dehydrochlorination of trichlorobutenes

Compound	Number of measurements	Initial concentration [mol l^{-1}]	k [mol^{-1} l min^{-1}]	Mean square error [mol^{-1} l min^{-1}]	Temperature ± 0.1°C
2,3,4-TCB	6	4.925×10^{-2}	0.130	0.004	1
	7		1.044	0.005	21
	5		6.730	0.030	40
2,3,3-TCB	7	1.6	0.016	0.0009	40
	7		0.031	0.001	45.5
	6		0.042	0.001	50
	8		0.113	0.007	60

Discussion

From the results it is apparent that dehydrochlorination of both 2,3,4-TCB and 2,3,3-TCB obeys the second-order reaction. This gives evidence that dehydrochlorination of both trichlorobutenes proceeds by E_2 mechanism.

Dehydrochlorination of 2,3,4-TCB proceeds at 40°C 436 times faster than dehydrochlorination of 2,3,3-TCB. As both starting compounds are isomeric trichlorobutenes and the end product is the same in both reactions (2,3-dichloro-1,3-butadiene), it is clear that the great difference between both reaction rates is due to the fact that in the molecule

of 2,3,3-TCB, two chlorine atoms are located at C-3. This is in agreement with the general knowledge [8, 9].

From the measured data, significant technological conclusions follow. To prepare 2,3-dichloro-1,3-butadiene from 2,3,4-TCB, dehydrochlorination should be accomplished at low temperatures because the monomer formed is essentially more reactive than for instance butadiene or chloroprene and at higher temperatures it can polymerize [10]. Under these conditions, however, dehydrochlorination of 1,2,3,3-tetrachlorobutane, which is formed besides 2,3,4-TCB [3], is after removing one molecule of hydrogen chloride practically stopped; *i.e.* when there are formed 2,3,3-TCB and other trichlorobutenes [11], which are not further dehydrochlorinated and contaminate the end product. When 2,3,4-TCB is the starting product, practically only 2,3-dichloro-1,3-butadiene is formed and the reaction is fast also at low temperatures. From this follows that from the technological point of view, it is necessary to remove 1,2,3,3-tetrachlorobutane from the crude 2,3,4-TCB by rectification most thoroughly.

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