REACTION OF 2,3-DIHALOGENOTETRAHYDROFURANS WITH SODIUM IODIDE*

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2,3-Dichlorotetrahydrofuran (*I*), 2-chloro-3-bromotetrahydrofuran (*II*), and 2,3-dibromo-tetrahydrofuran (*III*) react with NaI in acetone by a second order reaction under formation of elemental I_2 (or I_3^-); stoichiometrical ratio substrate: NaI is equal to 1 : 2. Reaction rate constants and activation parameters have been determined. The investigated 2,3-dihalogenotetrahydrofurans are not chemical individuals but form equilibrium mixture with their products after elimination of hydrogen halogenide. The composition of equilibrium mixtures was determined.
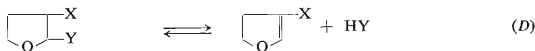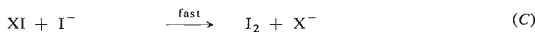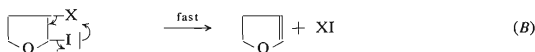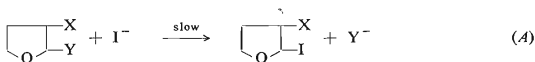
Compounds *I—III*, typical vicinal dihalogeno compounds in which α-halogen is activated by the ether-type oxygen, undergo on reaction with I^- elimination reaction in agreement with known experiences[1–3]. Its course was studied[2–4,5] in many vicinal dihalogeno compounds, and in the case of compound *I* the products formed and their yields[3] were also investigated. In agreement with these literature data the reaction scheme for substances *I—III* is proposed, expressed by equations $(A)–(C)$. The course of reactions of substances investigated in this paper is the same, the reactions differ only in their rate or activation parameters the knowledge of which enables one to judge objectively and compare the reactivity of the substances. The stoichiometry of the reactions corresponds to the consumption of 2 I^- per one molecule of dihalogeno derivative, but the reaction order is unit per I^- and per substrate, and the conversion curve corresponds to equation (I)

$$\mathrm{d}x/\mathrm{d}t = k(A_0 - x)(I_0 - 2x), \qquad (1)$$

where $x = A_0 - A = (I_0 - I)/2$ and A and A_0 are the actual and the starting concentrations of the substrate and I a I_0 are the actual and the starting concentrations of the iodide. Hence the reaction with the second particle must take place in another reaction step than the directing one in which the substrate reacts with the first iodide ion. On this basis, and with regard to the structure of substrates *I—III* in which both

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halogens are bound to a relatively rigid five-membered ring of tetrahydrofuran the course of their reaction with NaI may be explained by S_N2 substitution of the α-halogen of the substrate by the iodide ion according to equation (A), in agreement with other vicinal dihalogeno derivatives, although in the case of substances with a sole activated halogen the reaction order[2] may be lower than 2. A more rapid elimination of iodo halogen follows, which then reacts rapidly with I^- according to equation (B) and (C). As the starting substances are in fact only *trans*-isomers[3,7,8] the product of the reaction (A) will be a *cis*-isomer. Its accelerated decomposition follows, which may take place most simply by a cyclic rearrangement of electrons, as indicated in equation (B). This idea is supported by the ease of dissociation of the bond C_α—I, by the possibility of delocalisation of the positive charge on C_α in consequence of the neighbouring oxygen, and the possibility of contact of external electron orbitals of atoms I and X which are in one plane with both C_α and C_β atoms.

$$\text{(structure)} + I^- \xrightarrow{\text{slow}} \text{(structure)} + Y^- \qquad (A)$$

$$\text{(structure)} \xrightarrow{\text{fast}} \text{(structure)} + XI \qquad (B)$$

$$XI + I^- \xrightarrow{\text{fast}} I_2 + X^- \qquad (C)$$

$$\text{(structure)} \rightleftharpoons \text{(structure)} + HY \qquad (D)$$

2,3-Dihalogenotetrahydrofurans $I-III$ are not pure chemical individuals, but represent an equilibrium in the addition-elimination system according to equation (D).

The free hydrogen halide HY from equation (D) reacts in acetone medium very rapidly with Na^+ and forms insoluble chlorides or bromides[6] the quantity of which could be determined directly by weighing and used for the calculation of equilibrium concentrations which are shown in Table I. The correction of the NaI concentration was calculated which was caused by the conductivity of the released HI, and it could be approximately made more accurate in reverse by extrapolation from the graph of the conversion curve for the beginning of the reaction. On graphical treatment of the integral form of the rate equation (2) the corresponding rate constants given in Table I were determined.

$$k(t_2 - t_1) = \frac{2 \cdot 3}{2A_0 - I_0}\left(\log\frac{2A_2}{I_2} - \log\frac{2A_1}{I_1}\right) \qquad (2)$$

$$2k(t_2 - t_1) = 1/A_2 - 1/A_1 \quad \text{for} \quad 2A_0 = I_0 .$$

TABLE I

Reaction Rate Constants k of Elimination and the Content of Substrate in its Equilibrium Mixture A_r/A_0 at 20°C

Substrate	A_r/A_0, %	T, °C	$10^3 k$ l mol^{-1} min^{-1}
I (Cl, Cl)	90.3 ± 4.8	-25	4.19 ± 0.08
		0	11.75 ± 2.05
		25	46.5 ± 5.0
II (Br, Cl)	90.6 ± 2.2	-35	5.57 ± 0.08
		-25	11.0 ± 2.0
		0	17.4 ± 2.6
III (Br, Br)	89.3 ± 6.2	-35	158.0 ± 35.3
		-25	255.4 ± 23.0
		-15	333.0 ± 41.5

The effect of temperature on the reaction rate is evident from Fig. 1 in which the following values of the activation energies were used for the construction of straight lines: $E_I^{\ddagger} = 7.1$ kcal mol^{-1}; $E_{II}^{\ddagger} = 4.6$ kcal mol^{-1}; $E_{III}^{\ddagger} = 4.6$ kcal mol^{-1}, and $\Delta S_{I;248}^{\ddagger} = -48.4$ e.u.; $\Delta S_{II;248}^{\ddagger} = -56.8$ e.u.; $\Delta S_{III;248}^{\ddagger} = -50.1$ e.u.
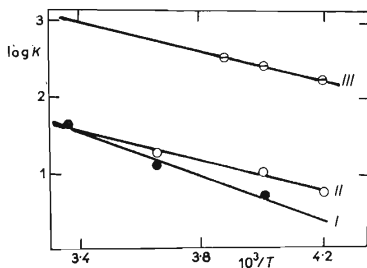

FIG. 1

Effect of Temperature on the Reaction Rate

EXPERIMENTAL

For the following of the reaction course the conductivity measurement of a NaI solution in acetone was made use of, in which the solubility of NaCl or NaBr, and the respective conductivities are negligible in comparison with NaI. For the measurement of conductivity a Conductivity Meter type OK-102 was employed with electrodes coated with platinum black. The measuring cell volume was 15 ml and it was temperated in an ethanol bath cooled with solid CO_2, or, for 25°C, in a ultrathermostated water bath. A NaI solution in acetone was introduced and the substrate added to it. After stirring the conductivity of the solution was measured and its course followed. The dependence of the conductivity on NaI concentration was determined experimentally for all temperatures used.

Chemicals: NaI was dried before use by heating it at 380°C for 2 hours. 2,3-Dichlorotetrahydrofuran (*I*) was prepared by chlorination of tetrahydrofuran[7,9,10] at 20—30°C and redistilled, b.p. 59·5—60·0°C/16 Torr; n_D^{20} 1·4833; d_4^{20} 1·3271. 2-Chloro-3-bromotetrahydrofuran (*II*) was prepared[11] by photochlorination of substance *III* at —20°C; b.p. 82·0—82·5°C/22 Torr; n_D^{20} 1·5212; d_4^{20} 1·6720; yield 64%. 2,3-Dibromotetrahydrofuran (*III*) was prepared by bromination of 2-chlorotetrahydrofuran[12,13] at 5°C; b.p. 91—93°C/17 Torr; n_D^{20} 1·5630; d_4^{20} 2·0419; yield 76%.

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